



João Daniel Rodrigues Carvalho **Caracterização de compósitos de polímero-cortiça através de testes mecânicos**

Mechanical characterization of cork-polymer composites through experimental tests

Apoio financeiro dos projetos

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Dissertação apresentada à Universidade de Aveiro para cumprimento dos requisitos necessários à obtenção do grau de Mestre em Engenharia Mecânica, realizada sob a orientação científica do Doutor Ricardo Alves Sousa, Professor Auxiliar com Agregação do Departamento de Engenharia Mecânica da Universidade de Aveiro.

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Palavras-chave

Compósitos, plástico reforçado, polímero, cortiça, testes mecânicos, impacto, tração.

Resumo

O presente documento reporta estudos relacionados com a combinação de cortiça a termoplásticos, e os respectivos testes de maneira a aferir a sua resistência mecânica. Polietileno, Policarbonato e ABS reforçados com diferentes percentagens de cortiça, para averiguar a possível aplicação do mesmo na região exterior do capacete. Para a correcta avaliação da potencialidade dos diferentes compósitos, foram efectuados testes de impacto e efectuados testes de tração uniaxial.

Neste trabalho, é apresentado um estudo para a utilização destes materiais para a região exterior de capacetes, como por exemplo de ciclismo, alpinismo, entre outros, aos quais foram adicionados diversas percentagens de cortiça para averiguar a adesão ao polímero e até que percentagem o novo compósito mantém características viáveis para o uso na aplicação pretendida. No caso do Polietileno, o seu estudo deveu-se à curiosidade científica no que toca à análise comportamental. A adição e respetiva mistura de cortiça com os três polímeros foi realizada a quente, tendo sido estudado quais as temperaturas ideais para cada tipo de polímero. As percentagens de cortiça estudados, variam desde os 10% até aos 50% total da mistura. O estudo foi efectuado através da criação de provetes, sendo assim viável o seu estudo nas diversas máquinas já preparadas para as dimensões do mesmo.

Por último, o estudo laboratorial desta dissertação pode ser dividido em duas partes distintas. Primeiramente, realizaram-se ensaios de impacto para se avaliar a quantidade de energia absorvida por cada um dos compósitos. Em segundo lugar, foram realizados ensaios de tração para ser possível retirar uma análise comportamental baseada na quantidade de cortiça adicionada, no que à tensão de cedência, módulo de Young e alongação máxima diz respeito.

keywords

Composites, reinforced polymers, cork, mechanical tests, charpy test, tensile test.

abstract

This document will review the mechanical tests that were conducted in order to evaluate and identify an optimization threshold for the relative mixtures between standardized polymers and cork. Polyethylene, Polycarbonate and ABS were mixed with varying percentages of cork grains to provide insight into the applicability of utilizing cork as a sustainable alternative in the helmet's outer shell without statistically significant deterioration of mechanical resistance.

This study was conducted to investigate the usage of a composite material composed by a mixture of polymer with cork, for helmets outer shell, such as cycling, motorcycle, alpinism, among others. The study was fulfilled by creating samples with different percentages of cork grains to evaluate the adhesive characteristics of the cork grains with the different polymers. Utilizing increasing percentages of cork grain from 10% to 50%. The addition of cork as a percentage of the total substance was increased in increments of 10 and the intermediate points are interpolated from the data collected. Even though the polyethylene is not a common material for the helmet outer shell, similar testing and evaluation was undertaken for purposes of scientific curiosity. Using the mixer available, the combination of both materials was conducted under heat.

Finally, the laboratorial experiments of this dissertation can be divided in two distinct parts: 1) An impact test was implemented to observe the quantity of energy retained by each sample mixture. 2) A tensile test, where it is possible to observe characteristics such as yield stress, maximum elongation or the young modulus.

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Acronyms list (by order of appearance)

1. BRIC – Brazil, Russia, India and China
2. ABS – Acrylonitrile butadiene styrene
3. PC – Polycarbonate
4. PE – Polyethylene
5. FRP – Fibre-reinforced plastic
6. GRP – Glass-reinforced plastic
7. CRP – Carbon-reinforced plastic
8. LDPE – Low density polyethylene
9. LLDPE – Linear low density polyethylene
10. HDPE – High density polyethylene
11. UHMW – Ultra high molecular weight polyethylene
12. CPC – Cork-polymer composite
13. UTS – Ultimate tensile strength
14. MSI – Melt flow index
15. ESAN – Escola Superior de Aveiro Norte

1. Introduction

1.1 Motivation

Living in the XXI century has increased our awareness for environmental issues like never before. Access to all kinds of information (internet, tv, social networks, etc) is helping people to understand that each action against the natural environment has a direct or indirect repercussion. This dissemination of information has led to the increased acceptance of the notion that it is the responsibility of mankind to preserve and respect nature in order to have a sustainable environment for the future.

Underdeveloped countries are growing at a faster pace when comparing to major economic power such Germany or USA. Countries including the BRIC nations, have an economic growth extending to roughly 5-10% per year (WHO, 2015); yet, the lack of capital and technological advancement leaves them with lower standards of living. In one measure, this is reflected in the economic decisions of the poorer echelons of society—for example, the need for economic means of transport result in many people being reliant on small motorcycles. This specifically detail raised awareness, because it is crucial to find alternatives to reduce the ecological footprint left by underdeveloped countries like Brazil and India as they undergo their period of high economic growth. One of the things that could be realised is the augment of materials utilized in the manufacturing of helmets to introduce renewable material, and this way try to implement a cutback on the amount of plastic used by each passenger.

To address this opportunity, a number of materials could be considered: cork, being a natural product widely used in Portuguese society and with a huge potential for industry is an option that this research has considered. Cork possesses numerous characteristics that make it a viable option for these purposes. These characteristics include: a great capacity for energy absorption (compression impact), an almost zero Poisson coefficient, and low density (Jardin, 2015). These characteristics become even more outstanding knowing that cork is 100% recyclable and it is a natural resource.

ABS and PC are the most common materials used for the outer shell of motorcycle helmets. These are highly resistant to physical impacts, cheap and very light. Both belong to the thermoplastic family, due to their behaviour of becoming liquid after the melting point – this is highly desirable in the manufacturing techniques involving injection moulding. Since both of these substances are highly resistant, in the moment of impact the blunt force can cause head or brain injuries; if the impact is too strong, the plastic will break releasing the energy to the fracture itself.

Being able to connect some of the cork features, e.g. cork returning to the initial form after impact, but still highly resistant, could allow the possibility to continue to use helmets even after undertaking strong impacts. Combining this pragmatic reason for the implementation of cork with the benefit of using a completely green/renewable material to reduce the ecological footprint is an aspiring objective to have for a dissertation.

1.2 Work goals

The focus of this Dissertation is to evaluate the mechanical behaviour of cork-polymer composites, the advantages and drawbacks involved in all of the process of manufacturing. In this work, it will be possible to gain a deep knowledge on the injection moulding process and the applicability of these composites for the outer shell of motorcycle helmets. A thorough and acute analysis on the thermoplastics (PC, ABS and PE) properties and all the cork properties relevant for this study will be drawn out and discussed with each of the merits and demerits of the substances in practical application for helmet safety.

1.3 Reading guide

This Dissertation is divided into five chapters:

Chapter 1— Introduction, presents and synthetizes the motivation and the goals as well as the context of the work.

Chapter 2— Referred to as the State of the Art, a brief overview of the important subjects addressed in this Dissertation is presented and supported by literary results. This bibliographic review also aims to help the understanding of the goals set forth in the dissertation.

Chapter 3— Materials and Methodology, intends to present and describe the methodology and operation steps, focusing in three areas; the inputs, the overall procedure and the outputs.

Chapter 4— Results and Discussion, aims to analyse and elaborate on the obtained results. This chapter highlights the differences in the results between the several samples tested.

Chapter 5— Conclusion, presents the most important conclusions of the work, highlighting the main ideas obtained through the performed testing. At the same time, perspectives and ideas for future work are presented.

2. State of the art

2.1 Overview on helmets

Motorcycle helmets are designed to protect against head and brain injuries during traffic collisions. (Rice, et al., 2017). According to (WHO, 2015) only 44 countries, representing 1.2 billion people, have helmet laws that meet best practice and apply a helmet standard. Motorcycle helmets can provide a reduction of 40% in risk of death and a 70% reduction of severe injuries when wearing a motorcycle helmet correctly. In fig.1, it is possible to visualize which countries meet the standards requirements and have a law for helmet use. The Asia and Pacific regions predominantly utilize small and inexpensive motorcycles, and will continue to dominate the market share with 84% quote for units sold in 2016. China will remain the largest national market, while India and Indonesia are two additional countries to take into account because they have the means and to produce and procure inexpensive motorcycles.

There is a strong correlation between median income and motorcycle demand until a certain point. In economies that are considered under-developed or developing, and are growing at an elevated pace, motorcycles are an attractive means of transportation. The combined benefits of a lower initial payment on the vehicle and the lower cost of gas due to fuel efficiency, make this the perfect transportation (Freedonia, 2013). From this data, and analysing fig.1, it is evident that in the majority of regions where despite the usage of motorcycles rapidly growing and seeing millions of people exposed to the dangers inherent in open aired vehicles, laws or helmet standardization do not frequently exist.

Due to this public health threat, it is crucial that studies like this dissertation are disclosed and disseminated to warn and alert the public concerning the dangers of not using a motorcycle helmet while driving.

Motorcycle helmet laws and helmet standards by country

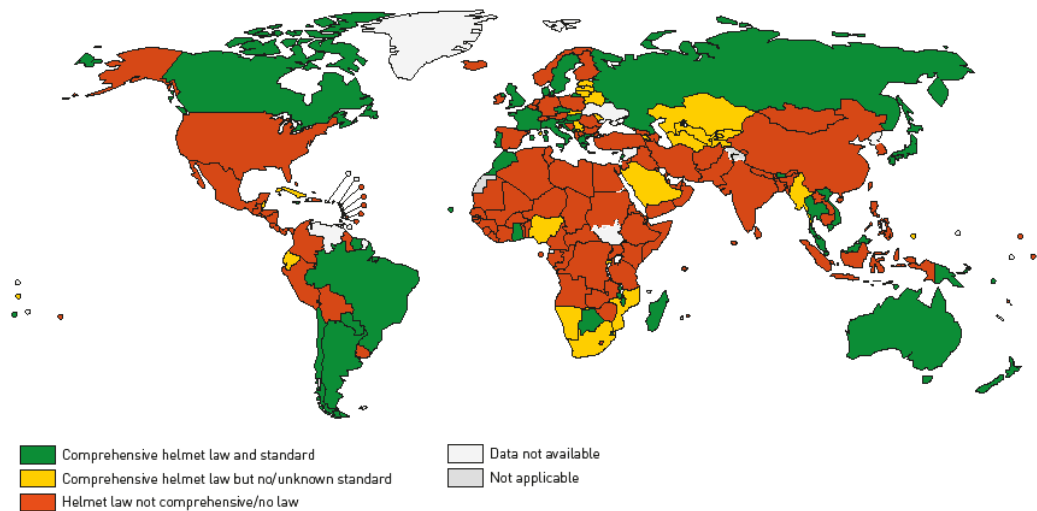


Figure 1 - Helmet laws and standards all over the world, (WHO, 2015)

2.1.1 Origins

This chapter provides a short historical briefing concerning the evolution of this safety apparatus. Starting with the Greek civilization, the helmet was used as a combat protection to reduce the possibility of strikes into the head, because in that time it certainly means death. An example of this accessory is in fig.3. As the societies evolved and the centuries pass, helmets suffered several modifications with the purpose of becoming more and more safe. This leads to the 20th century, where these modifications were more notorious due to the evolution of motorcycles. The lack of a safety device that provides real safety is astonishing. Because the only equipment that was available is an aviator bonnet, made of leather and usually worn with goggles. This was not a safety device; rather, the primary purpose was to keep the head comfortable and with the help of the goggles trying to minimize the outside weather conditions. In fig.4 is easy to get a full understanding of how meagre the aviator bonnet was as a means of protection and safety used in the early ages of motorcycling.

In order to change the paradigm around motorcycling and other sports which require helmets as a safety protection, engineers started to develop an accessory that combined comfort with more security. This way, (Newman, 2005) said that helmets evolved in an understanding of what it should do in protective terms, by fully acknowledge the biophysics of human head and a more resolved awareness of cinematic injuries in the skull.

It became obvious that a harder outer shell was needed to improve the safety. This was an immensely improved evolution when compared to the first leather bonnets. The leather was more rigid which gives an advantage on spreading the applied forces more homogeneously and in this way, reduce the affect at the point of impact. Through this application, the probability of having a skull fracture was dramatically reduced when comparing to the helmets that had previously been

in use. In order to fulfil this gap in security, engineers in the XX century started to develop a helmet constituted by some individual hard leather pieces, sewn to a hard fibre material crown section and lined with felt or fleece; which, only a few years later was replaced by an inner suspension. This improved the capacity of the helmet in absorbing and distributing impact energy through a wider area, therefore it was a development when comparing to the helmets that existed till then. Also had an improvement on reducing the inertial loads in the head, due to accelerations, by having a material that had high levels of absorption of kinetic energy. The introduction of these new materials and technologies significantly reduced the chance of having an intracranial injury derived from accelerations (Newman, 2005).

In the early 30's the first hard shell of modern motorcycle helmet was built. This was an evolution because for the first time, it was composed of several layers of cardboard glued and later it was constructed by impregnating linen with varnish resins, which allowed the cure into the final solid shape (Newman, 2005).

A few years later, a very important study was made saying that non-penetrating head injuries are caused by short-duration accelerations acting in the head and its contents (Holbourn, 1945). These acceleration injuries are the most common and dangerous form of injuries for motorcyclists and are often caused by blunt impact trauma rather than penetration incidences (Bosch, 2006).

The helmet as commonly seen and known today, was developed by (Roth & Lombard, 1953). An example can be seen in fig.2.

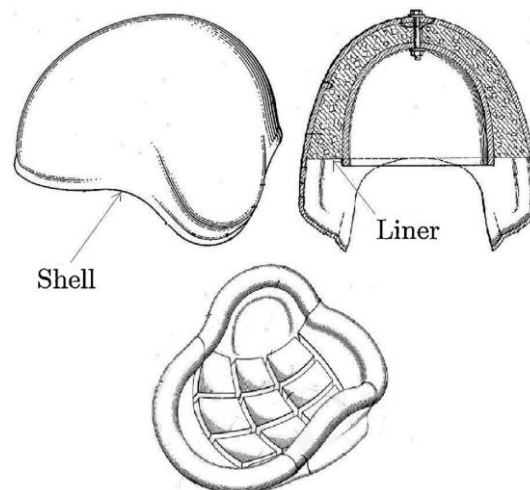


Figure 2 - Helmet from Roth and Lombard (Roth & Lombard, 1953)

The hard shell was made of 4 layers of fibre glass and several materials were used as padding material, such as expanded polystyrene (EPS) foam or polyurethane (PU) foam. Initially, PU foam was unanimously more used but thanks to EPS properties (cheap, readily available, relatively easy to manufacture and a good crushable energy absorbing material) it remains as the most used material in foam liners till this day.

In fact, helmets have the capacity of distributing the impact force over a very large area of the head and thus induce a reduction of the total force among the motorcyclist head as much as possible. Due to evolution of the helmets safety, currently this accessory can endure very strong impacts and has immensely improved the safety of people that utilize helmets during risk-bearing activities (N. Nemirovsky et al, 2010).



Figure 3 - Ancient Greek Corinthian bronze helmet – 5th century B.C, (Gold, 2012)



Figure 4 - Leather bonnet, (Antiques, 2012)

In other words, the technology around the perception of how the human head behaves in the time of impact is not being followed by the helmet brands. This is explained because brands are more interested in passing the control tests than innovating, so it should be the norms improving their standards in order to achieve evolution. Thus, the tests do not reflect integrally the real circumstances of accidents, as well as the bio fidelity of the skull or the movement imposed (Newman, 2005).

2.1.2 Functionality

The helmet is considered the best and most common protector for the head, because it can prevent or reduce injuries to the skull, or general skeletal structure, suffered during direct impact. Initially, the helmet was uniquely designated for the skull protection because fractures in the head are a common injury and this was a means to reduce the frequency of major incidents. Nowadays, and as the technology develops, helmets have another feature such as protecting the brain. The injuries in the brain can be even more common and severe than the ones in the skull so preventing and avoiding posterity problems or even death is necessary. Research and understanding of injuries

to the brain has significantly improves and more than trying to protect the skeletal components of the cranium, it is recognized that trauma to the brain without causing any bone fracture can have lasting impacts and previously had gone undetected. An auxiliary benefit of helmets used during cycling/motorcycling is related to reducing the contact of the head to external factors, such as wind exposure, rain as well as minimizing the contact of any foreign object or animal.

To get a full perception of how the helmet works, along with the characteristics and traits that are the most important components is important to divide the helmet in two major segments: 1) the hard-outer shell and 2) the inner liner.

The outer shell is responsible for distributing the impact forces to a larger foam area and this way leading to a higher energy absorption ratio through the foam liner due to the wider area involved. The greater the surface area involved in absorbing the impact, the less pressure is applied acutely to an individual location that can ultimately impact the individual underneath the helmet with adequate protection. Therefore, the probability of avoiding a head injury increases by reducing the total amount of force that reaches the head which results in vastly diminished likelihood to suffer a skull fracture (Shuaeib, et al., 2002b)

The second, and not less important, is the inner liner. This segment possesses materials with excellent energy absorption properties and when compared to the outer shell it ruptures more slowly which leads to a reduction of the inertial charge among the head. The direct consequence of this decrease is achieving a lower acceleration when the impact occurs, and thus reducing the likeliness of brain injuries due to induced accelerations. An explanation regarding the importance of this matter, is first and foremost that the probability of a brain injury is more likely than a skull fracture. Second, an example of this kind of injury is the closed head injury. In this injury, the skull is not fractured but the great head acceleration may cause brain injuries because of the relative movement of the brain inside the skull. For example, if the impact is on the front of the helmet the brain moves behind, squeezing the tissue near the impact site and stretching the tissue at the opposite end of the brain. This bounce of squeezing and stretching continues damaging until the acceleration inside the head subsides. This brain trauma is what causes concussions and can lead to very detrimental conditions without leaving any visible sign. In addition to this, other injuries can occur including instances ranging from the shearing of the brain tissue to bleeding in the brain, conducting to brain swell causing harder pressure against the inside part of the skull. This can be explained since the brain has space to move inside the skull and the contribution of inertia. So, in conclusion it is very important to keep the improvement of this safety accessory which could lead to chronic incapability or death not only in motorcyclists but a vast array of sports inclusive of: American football, ski, cycling and various other collision sports.

2.1.3 Design evolution

Design is invariably one of the most differentiating factors in branding these days. The competition is fierce and brands have the need to conjoin visual aesthetics with security. In this second aspect this chapter will focus, because the way helmet is designed has great importance in the mechanical response at impact (Aare, 2003). As described in *chapter 2.1.2*, liner softness and the thickness of the inner liner are variables that allow the head to decelerate at mild rate as it crushes the liner during the impact. Thicker foams remain in the plateau regime of the stress-strain curve for longer compression lengths (Kim, et al., 1997). The plateau stage and all other considerations pending on a stress-strain evaluation are described on *chapter 2.3.2*.

Although it is potentially advantageous to have a helmet with a thickness superior to pattern values (between 20 to 50 mm), there are limitations among the aesthetic level which cannot be overridden (Shuaeib, et al., 2002b). Moreover, this increment of thickness will have repercussions in the helmet volume level which is directly attached to the higher load the cervical spine will need to support (Huang, 1999).

Highlighting the design importance, (Bosch, 2006) refers that the optimal protective padding liner density depends on the impact site, where the protective padding liner density should be lower for the front and rear regions and should be higher for top region impact. (Gilchrist & Mills, 1994a) demonstrated that shell geometry has influence on the shell stiffness, as helmet shells are stiffer when loaded at the crown, since that site has a double-convex curvature and is distant from any free edges. Hence, the soft liner should be located in the crown region with the objective of compensating high shell stiffness and attempting to make helmet impact response site-independent. It is necessary to find an equilibrium between the thickness and softness of the inner liner, once is the most important characteristics in a collision. Besides geometry, the exterior finish of the shell is also important, influencing the friction against the impact surface, which has a tremendous effect on the rotational acceleration (Halldin, et al., 2001).

To achieve the standards, helmets are designed to reach a range of impact velocities (Mills, 1993). Due to ECE R 22.05, the absorbed energy test is made at the velocity of 7,5 m/s because the average impact velocity is between 5,83 m/s-8,33 m/s (Richter, et al., 2001). This means that for low-range velocity or high-impact velocity the helmet is not fully optimized, so is important to find alternative materials or designs that can address this flaw. Another case of how a security norm (Snell M2010, common used in USA) forces the helmet to be manufactured accordingly, is the penetration test which implies the helmet to be designed with enough stiffer shell to be approved, leading to higher acceleration values. This leads to a higher probability of the injured gain a cerebral lesion when compared to the probability of the helmet being penetrated in the moment of impact, which is significantly diminish (Hulme, et al., 1995).

In conclusion of this subchapter, is important to note that helmets should be designed to protect the human being and not simply to pass the tests. It is imperative that helmets be designed with worst-case scenarios in mind and not coincide with the requirements of average impact. While it is not realistic to expect every helmet to adhere to the highest standards, there needs to be options that can address heightened impact level under higher duress, and these qualifications and distinctions should be clearly communicated and highlighted as product features. In general, design needs to be improved, with a best comprehension of the biophysics of human head, the kinematic evaluation in cranial injuries or the biomechanical behaviour of the head in the time of impact. Helmets should be manufactured to bridge this, and not based on the appearance or the cost (Deck & Willinger, 2006).

2.1.4 Outer shell characterization

In the previous reading, a general idea of helmets has been provided— from its functionality to its design— this subchapter is of critical importance because this deviates from descriptive literature and is the centre topic of this Dissertation: This subchapter aims to clearly and succinctly define what a helmet is and should be and what the primary purpose it serves and how the research conducted in this dissertation is applicable.

The majority of the substance of helmets, especially the external facing portions, has a stiffer outer layer that is constituted by thermoplastic materials such as polycarbonate (PC) or Acrylonitrile-butadiene-styrene (ABS). There are also composite materials like plastic reinforced fibre (FRP), glass fibre reinforced with plastic (GRP), carbon reinforced with plastic (CRP), carbon fibre or Kevlar that might be found in the constitution of a helmet. The shells manufactured with thermoplastic materials show an isotropic behaviour (the same characteristics in every direction of the material) while the ones manufactured with FRP have an anisotropic behaviour in the shell plane (Mills & Gilchrist, 1992).

The most common thermoplastic material found in these cases is the GRP that consists of an epoxy resin reinforced with fibre glass. Commonly, thermoplastic shells are cheap when compared with the composite ones and show a fair mechanical performance (Tinard, et al., 2012a). Carbon fibre and Kevlar are usually used in high end helmets (Cernicchi, et al., 2008).

The outer shell can be characterized through the follow functions:

- To spread the impact load on a more extensive area, reducing the local stresses where the helmet was hit. This way, the energetic absorption capability is increased thanks to a higher energetic efficiency due to a higher area involved in the load distribution;
- To prevent the penetration of pointy objects in the helmet that otherwise could cause harm to the cranium;

- To serve as an interior coating to avoid disintegration in cases of abrasive contact with the pavement or another impact surface. This is of critical importance once the foams used as interior coating have low resistance to penetration and abrasion, as studied by (Beusenberg & Happee, 1993). Every damage shown in the internal layers of a helmet happens as a consequence of a crack in the external rigid shell, that increases the probability of injury (Beusenberg & Happee, 1993). Another important factor is that the external layer, the helmet shell, reinforce the integrity of the helmet when multiple impacts occur, being an indispensable structural component of this safety tool;
- To absorb the first hit in an accident. Only a fraction of energy is absorbed. Through the literature, these energy values are very inconstant once there are differences in the performed tests, in terms of velocity or materials used and its properties. Besides that, (Mills, 1995) affirms that the helmet shell is capable of absorb 30% of the total energy of impact. (Gilchrist & Mills, 1994a) claims that these values may vary between 10% and 30%. Recent studies show that the energy absorption varies only between 12% and 15% (Ghajari, 2009b).

To meet the other subject discussed in this subchapter, helmet shells made by high end composite materials are progressively replacing the ones made from thermoplastic materials. As previously stated, the last ones are significantly more expensive, raising the discussion of its cost-benefit.

During an impact, when the coating foam breaks completely, the energy that was not been absorbed will be transferred to the head and the forces occurring there will be very high. This impact loads would be lower if the device had some mechanism to absorb extra energy. In this specific case, the adding of another kind of materials in the external shell, such as composites. These materials show better characteristics when compared with thermoplastics once they have better capability to absorb energy through the fibre rupture, break of matrix and laminar fracture (delamination), depending on the subjected tensions in the material. Thanks to that, the major advantage of the usage of composite materials is related to the capability of this material to absorb energy through the rupture when compared with thermoplastics. The thermoplastic material can absorb energy through the material bending and permanent plastic deformation, but has limited ability to absorb past the rupture point (Cernicchi, et al., 2008) but these values are lower when compared with the composites.

The stiffness of the shell has a relevant influence in the general performance of the helmet. The FRP shows higher stiffness than the PC as demonstrated by (Beusenberg & Happee, 1993), where the energy was almost completely absorbed by the foam deformation.

Another example is the one from (Gilchrist & Mills, 1994a) that claims that the helmet shells made of composite materials show lower deformation than ABS. This author also refers that,

besides this, the impact forces associated to the composite helmets are higher than the ones made of thermoplastics.

This behaviour cannot be reached in a low energy impact level, showing that the composite materials need a high impact velocity when compared with thermoplastics (Mills & Gilchrist, 1991).

As previously referred, the helmet shells constituted by composite materials have a high stiffness which may have a negative impact in the induced acceleration for a low energy level, where there is no rupture of the fibrous binding, because the high impact absorption capability of a composite is based on this rupture. On the other hand, for stronger impacts, the composite shell shows advantages once it is able to absorb the impact energy until the final rupture (Kostopoulos, et al., 2002). Another parameter previously referred was the composite delamination but, in order to this factor to happen, there is a need for very high impact energy. Furthermore, the impact forces, when compared to thermoplastic materials, are tremendously superiors.

2.2 Thermoplastic materials

2.2.1 ABS

ABS is the short abbreviation of acrylonitrile butadiene styrene, a copolymer with the chemical formula of $(C_8H_8 \cdot C_4H_6 \cdot C_3H_3N)_n$, fig.5, and the proportion of each element varies towards the desired application. Regarding the ABS samples that are going to be presented in this dissertation, they are composed by 95 – 100% of ABS, 0-3% of typical stabilizer and 0-5% of typical lubricants. The information is provided in the ABS technical file, available in the Appendix A.

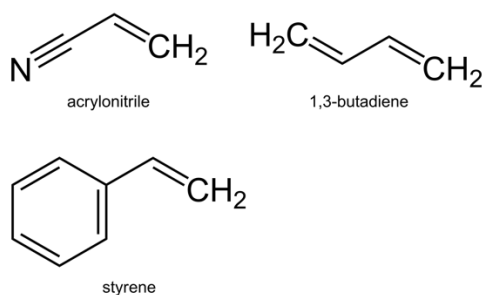


Figure 5 – ABS chemical structure, (Wikipedia, 2017)

ABS is normally polymerized through the process of emulsion, but there are other processes like continuous mass polymerization, suspension, solution or bulk polymerization (BorgWarner Chemicals, 2015).

This polymer is an opaque thermoplastic, which can be heated, cooled and re-heated again with no significant degradation. Since it is a thermoplastic material, it means that it is recyclable and a common way to produce ABS is from another ABS plastic.

The characteristics of ABS are multiple, starting from its strong resistance to corrosive chemicals or physical impacts. It is also easily processed. Another interesting feature for this material on the scope of this study is the low melting point, which makes it simpler to use in injection moulding manufacturing processes as well as 3D printing (Mechanisms, 2017).

Among the most common applications of ABS are golf club heads (due to good shock absorbance), automotive trim components, enclosures for electrical and electronic assemblies, protective headgear and Lego's (Wikipedia, 2017).



Figure 6 – Fender, (Pandey, 2017)



Figure 7 - Headgear, (Array, 2017)

2.2.2 PC

Polycarbonate is an amorphous transparent thermoplastic, a particular kind of polysaccharides (long chain polymers), composed by functional groups of carbonates ($-\text{[CO-O-pPh-C(CH}_3\text{)}_2\text{-pPh-O)]}_n$). The main features of this polycarbonate is the low crystallinity, colourless, highly resistant to impact, good dimensional stability and good elastic properties. It is one of the three most important engineering plastics (the others are Polyamide and Polyacetal) (Hassan & Yean Jwu, 2005). PC is made from the distillation of hydrocarbon fuels into lighter groups which are combined with other catalysts to produce plastic (as referred before, processes like continuous polymerization).

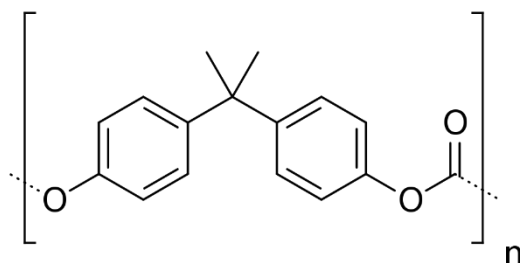


Figure 8 - PC chemical structure, (Wikipedia, 2017)

PC is commonly used for plastic lenses, medical devices, headgears, automotive components, digital disks and other features. In the following diagram, it is an example of polycarbonate impact resistance compared to other polymers.

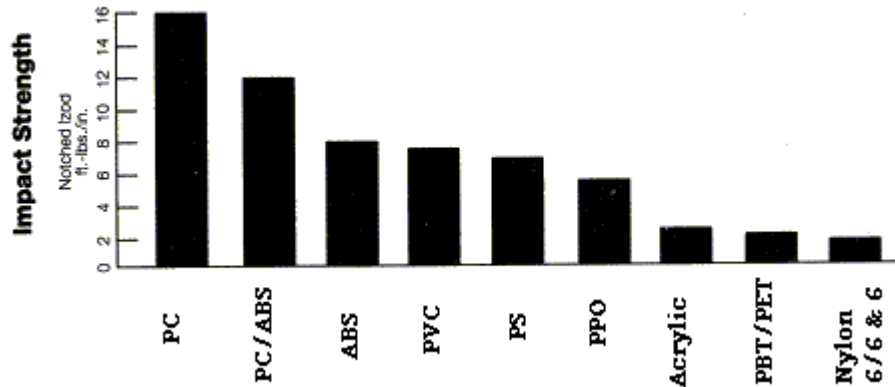


Figure 9 - Impact strength, (Mechanisms, 2017)

2.2.3 Polyethylene

Polyethylene is thermoplastic polymer represented by the chain: $(\text{CH}_2\text{-CH}_2)_n$, being one of the simplest forms of polymer. Due to its world production, is the cheapest and also one of the most commons. It is obtained by ethylene polymerization, but the production of this polymer can be from several polymerization reactions, depending on which final form is pretended.

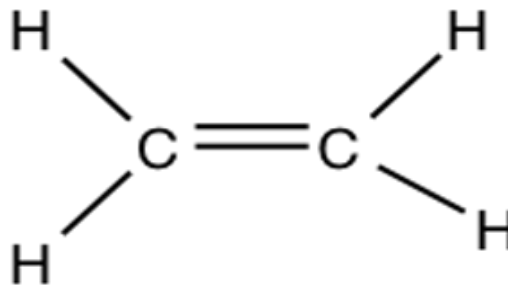


Figure 10 - PE chemical structure, (Study.com, 2017)

Inside the PE structure, it is possible to obtain several forms of PE, such as:

- **Low density polyethylene (LDPE)** is a very flexible material with very unique flow properties that makes it particularly suitable to plastic film applications like shopping bags. LDPE has high ductility but low tensile strength which is evident in the real world by its propensity to stretch when strained;

- **Linear low density polyethylene (LLDPE)** is very similar to LDPE with the added advantage that the properties of LLDPE can be altered by adjusting the formula constituents and that the overall production process for LLDPE is typically less energy intensive than LDPE;
- **High density polyethylene (HDPE)** is a strong, high density, moderately stiff plastic with a highly crystalline structure. It is frequently used as a plastic for milk cartons, laundry detergent, garbage bins, and cutting boards;
- **Ultrahigh molecular weight polyethylene (UHMW)** is an extremely dense version of polyethylene with molecular weights typically an order of magnitude greater than HDPE. It can be spun into threads with tensile strengths many times greater than steel and is frequently incorporated into high performance equipment like bulletproof vests (Mechanisms, 2017).

In this dissertation, the PE used for the trials was the HDPE, and the results are possible to be followed upfront.

2.3 Cork

This section will cover numerous topics related to cork: Starting with a brief explanation of cellular materials (where cork is inserted in), this will then be followed by the *Origin and Growth*. Subsequently, it will delve into all the process of the development of cork tree and extraction. *Properties*, explaining the composition, changes when compressed and the summary of the best features. *Manufacturing and production* gives an idea on the economic potential of this material as well as all the stages of industrialization. In *Applications*, it will be described in which areas of business the cork is commonly used. At last, a brief explanation on *Viscoelasticity*.

Cellular materials have been used for thousands of years, with a very diversified range of application. For example, wood for building structures, cork for thermic insulation or bone in the manufacturing of tools. These present a combination of singular properties like good thermal, acoustic insulation, high stiffness, big capability of absorbing energy and high yield strength in relation to its mass.

Almost all materials can be used to form cell structures. Most polymers can readily form a cellular material by injecting pressurized gas into the polymer in the liquid phase. An alternative process is to mix chemicals that release carbon dioxide with the polymer granules prior to the heating cycle, which are then retained as bubbles within the polymer (Gibson & Ashby, 1997).

2.3.1 Origin and growth

Cork is a natural cellular material which is extracted from the cork tree (*Quercus Suber L.*), a noble and truly special genre that grows specially in Mediterranean regions as Spain, Italy, France,

Algeria and predominantly in Portugal where there are 730 thousand hectares of cork tree, as well as a cork industry of significant economic impact (Associação Portuguesa da Cortiça, 2009).

The cork oak development is slow but is a long growing tree which can live generally from 250 to 350 years, being only active for cork extraction till 150 or 200 years. During this period, and in a minimum of a 9-year interval; which, given the weather conditions of Portugal, is the minimum time for the tree to have a 27mm of thickness (for the proposed criteria of cork stopper industry). Once matured to a desired thickness/volume, the cork is extracted by cut and pull-out about the form of boards.



Figure 11 - Cork boards extraction, (Fortes, 2004)

In fig.11, it is possible to see an example of cork boards during the removal. The extraction is normally during the summer, because the radial growth of the tree occurs between March and October, with the highest growth rate in May and June.

After the cork removal, the layer that gives rise (phellogen) is destroyed. However, the cork tree has the ability of regenerating, inside the inner bark a layer named traumatic phellogen, which results from the removal, giving birth to a new layer of cork cells. After the removal, the phellogen layer is created after 25 to 35 days and past 50 days the first cells of cork start being produced. This regenerating capability allows the sustainable exploitation of the cork tree during its life through a succession of extractions over the roughly 150-200 years of fruitful growth. These cuts are made by tangential and longitudinal cuts in the bark tree with the help of an axe.

Around the period in time which the tree reaches 20-35 years old, the time when the tree accomplishes the dimensions proposed (diameter between 20-25 cm), the first debarking occurs. This incident releases the virgin cork. This is a highly irregular structure and surface, due to the

fractures from the tangential strain of the trunk radial growth. This first shipment is not adequate for stoppers, so its use is exclusively for the manufacture of agglomerates.

The second generation is named “secundeira” (in Portuguese), and although it presents a better quality on the surface and structurally, is not sufficient. In this generation the resulting strains from the trunk growth are still considerable, leading to the appearance of clefts denying the usage in the stoppers industry.

At last, after the removal of this layer is finally formed and for the consequent generations a cork layer with a fairly uniform thickness, few clefts and shallow depth named *amadia cork*, and is the main raw material for the industry. The first extraction of this type of cork happens normally between 40 to 50 years of the cork tree.

As referred, the virgin cork and secondary, as well with the waste of *amadia* are used for the preparation of granules (Pereira, 2007).

There are two basic types of agglomerates, the black agglomerate, constituted only by granules of cork and the compose agglomerate, cork granules that also have adhesive materials as agglomerating resin, linseed oil or rubber.

2.3.2 Properties

Cork, as a natural and cellular material, has typical properties which are common to all this kind of comparable materials. When it is compressed, its stress-strain curve has three distinct zones. An example of this is in fig.12.

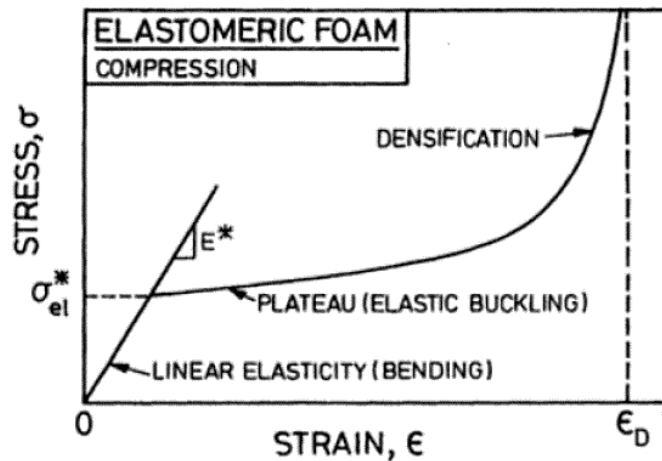


Figure 12 - Compression scheme of cork, (Gibson & Ashby, 1997)

For small deformations the material has an elastically linear behaviour. After this, it progresses to a zone of higher deformation but the strain is mainly constant (plateau). This stage is due to the buckling of the cell walls. Finally, it follows a region of densification, during which the cell walls are crushed against each other and it is observed a strong increase of the strain to small deformations (Gibson & Ashby, 1997).

As other several anisotropic materials (when the mechanical properties are different in various directions) cork has in each layer a different disposition of the cells. The first one to notest the anisotropy was Hooke in the century of XVII and it is represented in his book named *Micrographia* (fig.14). This description was posteriorly verified for several authors. With these observations, is possible to characterize three main directions that define the orientation of the cork in the cork tree (fig.13):

1. Radial direction (through the trunk radius);
2. Axial direction (parallel to the trunk);
3. Tangential direction (tangential to the circumference of the trunk).

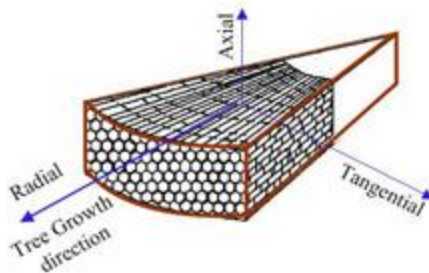


Fig. 1 Illustration of the three main directions of the disposal cell in a section of cork

Figure 13 - Cork main directions, (Kermezli, 2017)

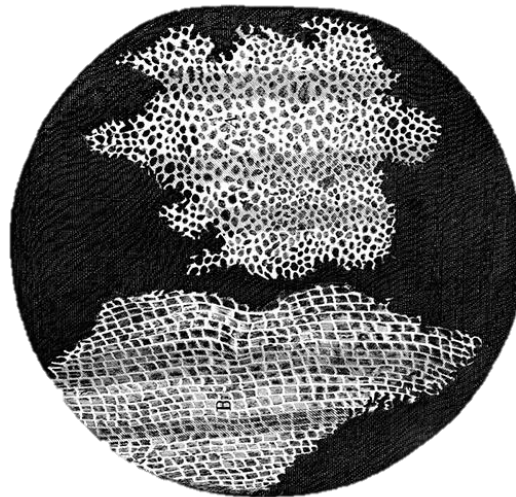


Figure 14 - Hooke's drawings on cork structure, (Hooke, 1965)

Cork cells present on average a hexagonal prism structure, although the polygon can have between 4 to 9 sides but normally has 5 to 7 (fig.15).

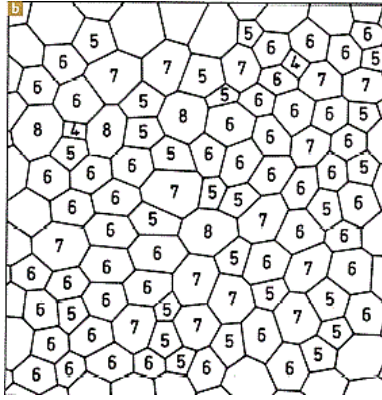


Figure 15 - Number of sides of cork cells, (Fortes, 2004)

Also, the average height is 45 microns, the side of the cell is in average 20 microns and thickness of the cellular wall 1 micron. The amplitude ripple is 5 microns (Gibson & Ashby, 1997). The cells are piled up in columns, where the axis has radial direction. Normally they possess 14 adjacent cells and there is no direct correlation between the height of the cork cells in the adjacent columns. Thus, cells present themselves wavy due to the fact of the new generated cork cells increasing the compression strain on the ones already formed, which derives from the buckling of the side walls.

In cellular materials, cork is constituted by closed-cells who form in space a three-dimensional structure. Cellular walls are formed mostly by suberin, a biopolymer of lipid character, which provides many of the cork mechanic characteristics such as low permeability, low thermic and acoustic conductivity and the most important to this dissertation an absorption capacity and power dissipation. Due to this, the volume fraction of solid material is 15% of the total volume, and with a relative density of 200 kg/m³.

In sum, cork presents the several properties:

1. Good fire resistance;
2. Low absorption ratio of liquids;
3. Good chemical inertia;
4. High coefficient of friction;
5. Great energy dissipation capacity (vibration);
6. Great energy absorption capability (impact);
7. Low Poisson coefficient;
8. High deformability and low resistance to deformation;
9. Low density;
10. Low thermal conductivity.

2.3.3 Manufacturing and transformation

The cork oak has an important contribution for several economies down the Mediterranean, occupying a total area of 2.139.942 hectares. Portugal has the largest area of cork oak forest in the world with 34%, corresponding to 736.775 hectares, which represents 23% of the total national forest of Portugal. This makes cork oak as the most representative specie of the entire Portuguese forest.

Área mundial de montado		
País	Área (hectares - ha) *	Porcentagem
Portugal	736.775	34
Espanha	574.248	27
Marrocos	383.120	18
Argélia	230.000	11
Tunísia	85.771	4
França	65.228	3
Itália	64.800	3
Total	2.139.942	100

* Fonte: Portugal: IFN, 2013; Espanha: MARIM, 2007; Itália: FAO, 2005; França: IM Liège, 2005; Marrocos: HCEF Maroc, 2011; Argélia: EFI, 2009; Tunísia: Ben Jamaa, 2011.

Figure 16 - Area of cork oak, (APCOR, 2016)

The cork oak area has grown about 3% in the last 10 years as a consequence of some reforestation programs. More than 130,000 hectares were planted in Portugal and Spain in the last 10 to 15 years, with a density of approximately 120 to 150 trees per hectare. The average density is approximately 80 trees per hectare, although it can reach 120 trees or more, and 5% of the total area can be used for cereal crops such as wheat, barley or oats and 40% for pasture (Associação Portuguesa da Cortiça, 2009).

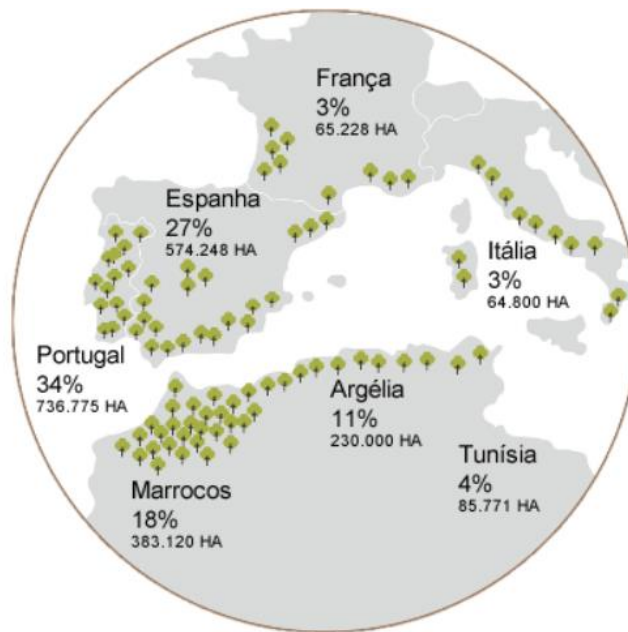


Figure 17 - Visual cork oak area, (APCOR, 2016)

Portuguese leadership in the cork industry has made Portugal a significant player in the global market for cork in the economic domain, being the biggest producer with more than 150 thousand tons annually, which represents a staggering 52.5% of the global production. In relation to this ability to produce cork in mass, Portugal has taken advantage of their comparative advantage such that Portugal is leader regarding exportation of cork with an approximate value of 63% (937,5 M €) (Division, 2016). This year represented a growth of 4% comparing to the previous, the best year ever in cork exportation. This industry exports 90% of the production to 133 countries, and from this number, 72% corresponds to wine stoppers. Following appear the construction materials in cork, with 25%, and new applications represent only 3% but with an elevated growth potential. The trade balance is highly positive, being the difference of 763,9 M €. Regarding Portuguese economy, this represents 7,5% of the total exportations, which makes cork one of the most important economy boosters (APCOR, 2016).

Cork industrial processing is divided into 4 sub-sectors:

- **Preparation:** takes care of operations after the extraction of the cork as the baking, the tracing, trimming, sorting and baling;
- **Transformation:** it is mainly dedicated to the production of natural cork stoppers and discs, from the board;
- **Granulation:** it deals with the grinding of the cork of inferior quality and the manufacture of stoppers (waste from preparation and transformation activities);
- **Agglomeration:** takes care of the production of pure expanded agglomerate (black) and agglomerate compound (with the addition of binders), which is the basis of several

products (corks and particle boards, floor coverings and walls, insulation joints) (Gonçalves, 2009).

The manufacturing sector occupies the leading position in Portugal, and has the largest industrial and manufacturing capacity in the world for processing cork, transforming around 70% of cork, and exportation of the processed products.

One of the characteristics that makes this material so interesting, is the fact it is totally recyclable. This will be one of the highlighting points during this dissertation, as well as the study regarding the tensile strength and the impact energy absorption.

2.3.4 Applications

Being 100% natural, cork presents unique properties that no technology has ever been able to imitate: it is light to the point of floating, waterproof, insulated, flexible and compressible, resistant to friction, temperature and time wear, hypoallergenic and comfortable. As a result of a significant investment in R&D and innovation, the potential of this raw material is as infinite as the imagination. And technological advances allow you to enjoy its high technical performance like never before (Amorim, 2017).

Some of the applications are illustrated on the images below:

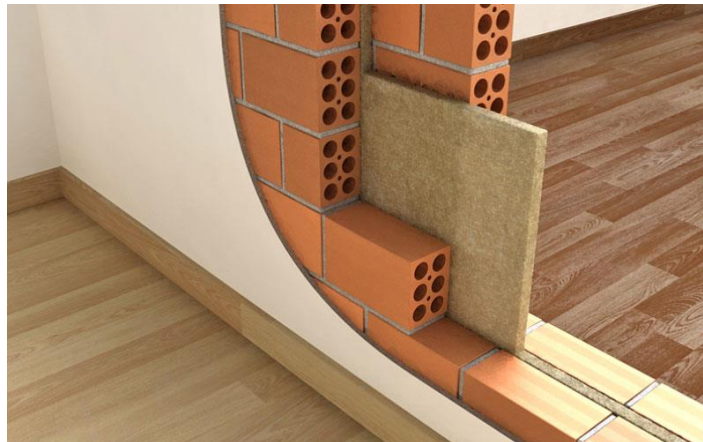


Figure 18 - Cork Insulation, (TLVE, 2017)



Figure 19 - Cork stopper, (Amorim, 2017)



Figure 20 - Fashion applications, (Moda, 2017)

2.3.5 Viscoelasticity

In this sub-chapter it will be briefly discussed a cork characteristic that is widely spread over literature. Viscoelasticity is a property that relates elasticity with viscosity as the name implies. This characteristic of cork can be defined by a strain that does not follow immediately the tension imposed, once the molecular disorders provoked by the tension on the surface of cork do not occur instantaneously. In elastic materials, when materials immediately tend to adjust to its initial configuration, whilst the viscoelastic materials this does not happen. Viscoelasticity is highly susceptible to temperatures and strain rate.

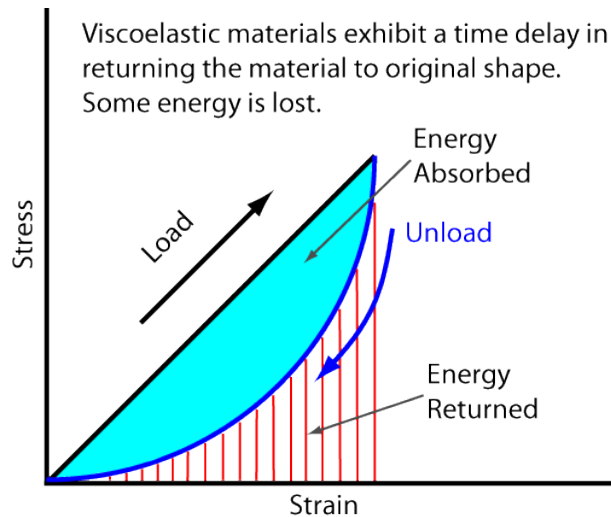


Figure 21 - Viscoelastic behaviour of cork (UTA, 2017), aka Hysteresis

3. Materials and methodology

3.1 Materials

Cork grains were supplied by Amorim cork composites S.A., and the particle size is 0,5-1,0mm (small grains). There was also the possibility to use larger grains (2,0-4,0mm), but since the sample geometry is relatively small the compactness of the grains would not be guaranteed.

The polymers (PE, ABS and PC) are in the form of pellets and the particle size is: 2,0-4,0mm. ABS has the specificity of having a pre-treatment to enhance the characteristics for the outer shell helmet use. The datasheet is available in the Appendix A.

The table below announces the materials main characteristics, and the adopted reference used for the rest of the dissertation.

In fig.22 & 23 it is possible to observe the polymers used in the experimental work as well as cork powder.



Figure 22 - ABS, PC and PE pellets



Figure 23 - Cork powder

In the next sub-chapter, the meticulous approach to build each one of the samples will be highlighted. Since the objective is to have samples with different percentages of cork to assess the performance of the materials at varying proportions of traditional polymers and cork it is key to ascertain correctness in measurement of quantity and performance for each sample tested. This will allow greater understanding to the composite response to the addition of cork to the alternative polymers.

Table 1 - Material description and acronyms (Matweb, 2017)

	Density (kg/m ³)	Adopted reference	Grain size (mm)
Cork	180	Cork	0,5-1,0
Polyethylene (HDPE)	915	PE	2,0-4,0
Polycarbonate	950	PC	2,0-4,0
Acrylonitrile butadiene styrene	1020	ABS	2,0-4,0

3.2 Sample production

In this chapter, it will be possible to evaluate approximately two months of laboratory work. It is a mechanical and methodical process to reach the final objective of having CPC (*cork-polymer composites*) specimens with the geometry below (fig.24 & 25).

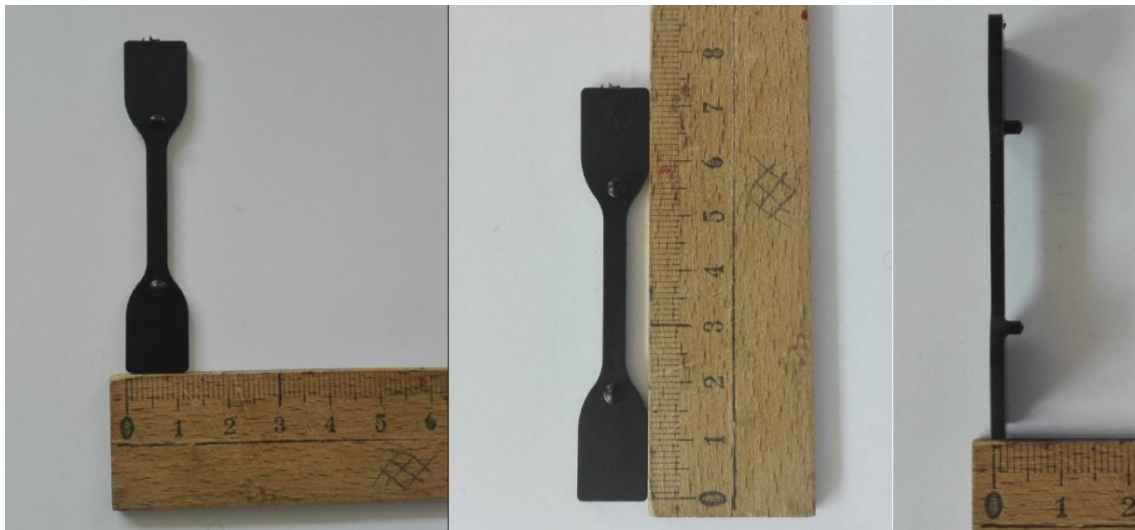


Figure 24 - Specimen dimensions



Figure 25 -CPC specimens of PE, PC and ABS respectively

The focus of the experimental campaign is to study the interference of adding cork to the mixture, in intervals of 10% comparing to the starting point of having a 100% pure polymeric sample in contrast with the maximum of 50% of cork in the mixture.

This will imply the manufacturing of 108 samples, 6 for each mixture. As further explained in *chapter 4*, the sample manufacturing will allow the execution of tensile and Charpy tests.

The samples manufacturing process are grossly related to the work of a mixer (*Plastograph EC Brabender*) and a compression moulding injection machine (*HAAKE Minijet II*), respectively (fig.26).



Figure 26 -Mini Injector HAAKE & Mixer EC Brabender

The first step of the preparation is to define the different weights for the samples, since densities (table 1) differ for each polymer although the volume stays fixed (mixing chamber volume: 20 cm³). This is done with the help of a scale (Kern FCB, max wt: 6100 gr; d: 0,02 gr).

The second step of the preparation is to obtain the raw material CPC, and this is done in the mixer (fig.26). The function of this machine is through shaft rotation and heat, combine both materials (polymer and cork) into a single homogeneous substance with singular properties.

In figures (27;28;29), it is graphically explained the weight of the different material combinations inserted into the mixing chamber. It is important to refer that this is not the weight for each sample. Based on the experiments, it is possible to estimate that for each mixing process is enough material for 7 samples.

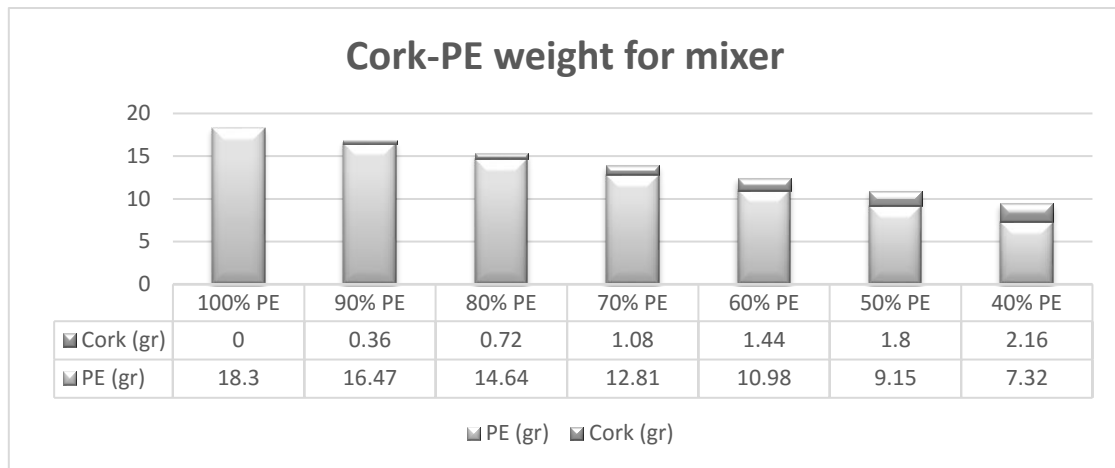


Figure 27 – Cork and PE weight for mixing chamber

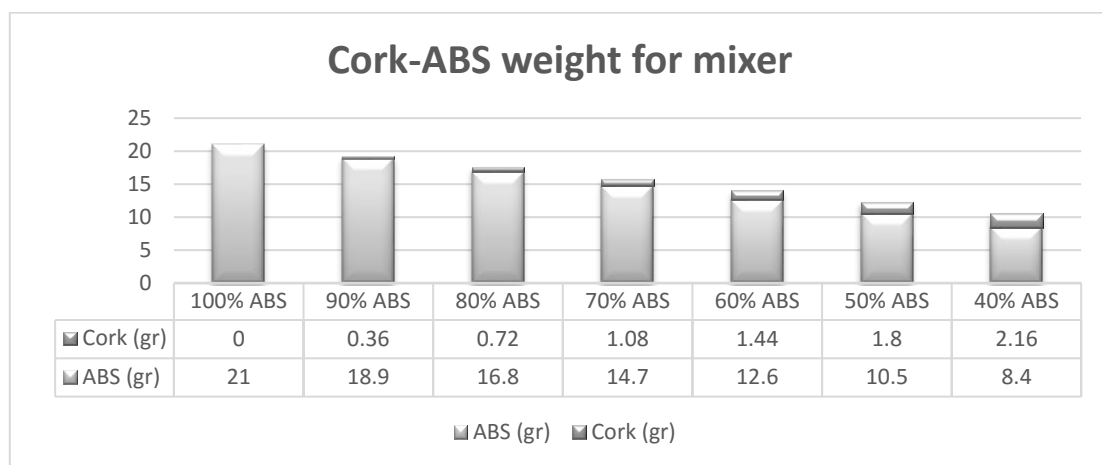


Figure 28 - Cork and ABS weight for mixing chamber

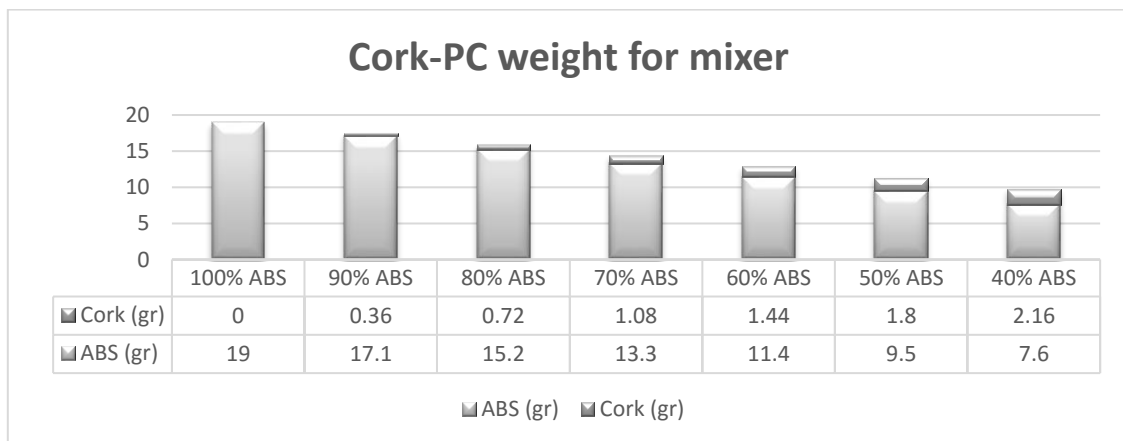


Figure 29 - Cork and PC weight for mixing chamber

Directly connected to the chamber, there is a nozzle where it is possible to pour down both materials (in this particular case, polymer and cork) and then a stick is inserted to keep the mixture contained in the chamber. Both the nozzle and the stick are represented in fig.30 & 31.

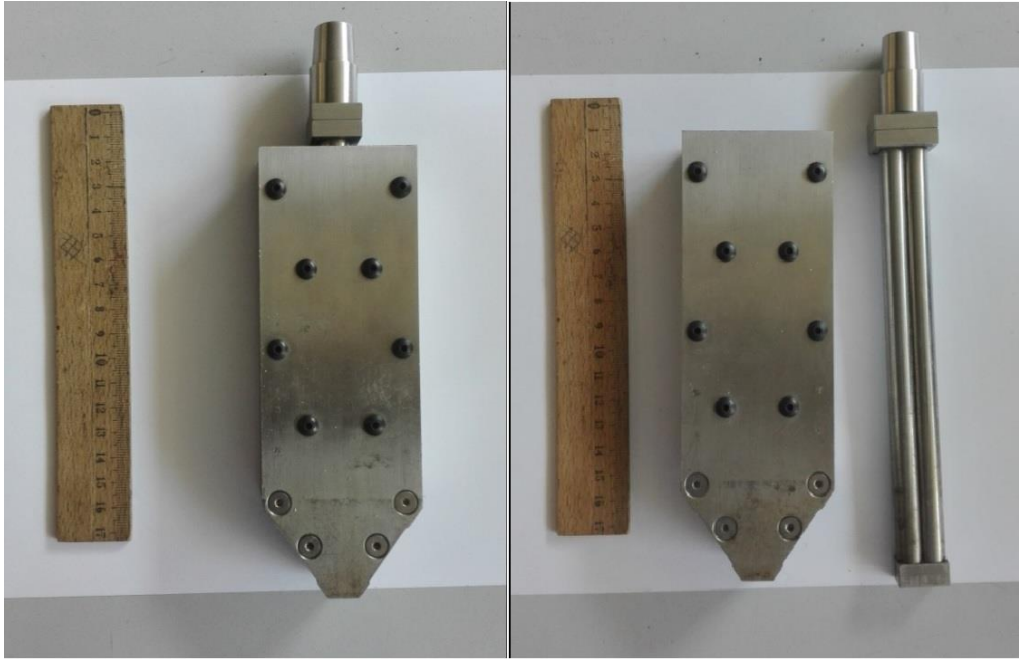


Figure 30 - Nozzle and stick

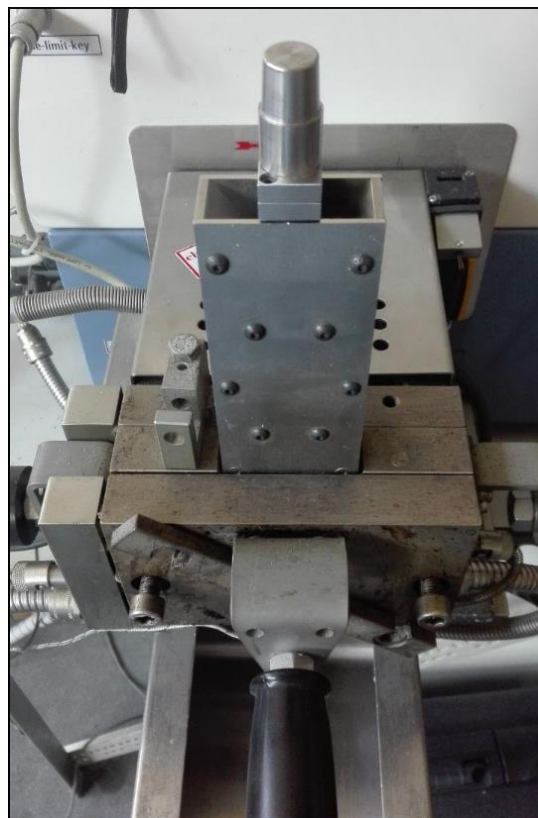


Figure 31 - Nozzle and stick inserted in the mixer

The temperature upon the mixing chamber differs for each polymer since they have different melting-point temperatures (Matweb, 2017). To refer that the main concern in the temperature used was the melting temperature of the polymers, since it is the most important to guarantee the homogeneity of the samples. Cork characteristics were also taken into account, and that is the

reason why we tried to have the lowest temperature over the mixing chamber possible. The structural properties of lignocellulosic materials like cork are highly dependent on temperature. Thermal decomposition of cork has been studied by thermogravimetry (Rosa & Fortes, 1988) and the results reflect a decrease on the mass by 30% when heating at 300°C and less than 10% at 200°C (Rosa & Fortes, 1988). In terms of chemical degradation, it has been shown that cork can be heated up to 250°C without any irreversible change in its composition.

Having this information regarding cork, it became necessary to avoid using temperatures above the minimum necessary to get homogeneous samples of CPC. From literature, it was possible to get some information regarding which temperatures should be set up in the mixing process. The temperatures used for each composite are described in table 2.

Table 2 - Mixer temperatures set up for each CPC

CPCs	Mixing temperature [°C] & shaft rotation [rpm]
ABS	210 °C / 50 rpm
PE	150°C / 50 rpm
PC	230°C / 50 rpm

For ABS, the temperature used was 210°C, the lowest value from the melting point interval data given by the manufacturer, which can be found in the Appendix A. For PC, and since it was not available a technical file, this discovery process was by trial and error. Initially, the same temperature as ABS was used which was soon realized was at a lower point than required, since cork and PC didn't match well together. After some experiments, the temperature used for all the samples was 230°C. It was decided to start the experiment with PE because it possesses the lowest melting temperature of the three, PE has an estimate melting temperature of 150°C, which has been set in the mixer (Fernandes, et al., 2011). The other key intervenient, is the velocity of the veins inside the mixing chamber. In all these cases the velocity used was 50 rpm. Each setup takes about 8 minutes to be concluded, and after it is necessary to remove the mixture. This is made by parts, since the mixture remains in an area known as the mixing chamber which is connected to two steel plates of 15 cm thickness containing the heat and supporting the chamber. This area of the machine is then modular (fig.32), to facilitate the fast removal of the CPC from its interior.

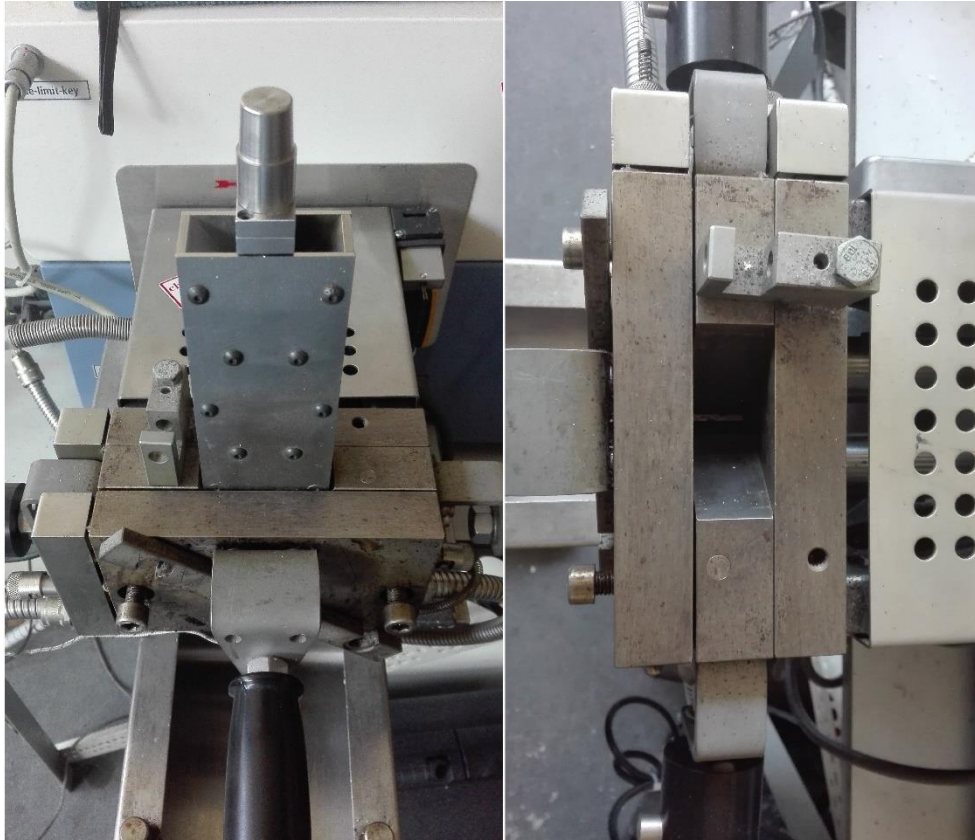


Figure 32 - Mixer nozzle and chamber



Figure 33- Modular parts of the mixer

To extract the material from inside, the job was done with the help of a spatula since the material was still melted.

After repeating this process for every CPC's proposed to study, it is now possible to have a first reflection on the work to come. Since these are thermoplastics, the case of re-heating is not a negative aspect. The three polymers are classified as thermoplastics (opposed to thermoset, which can only be heated once), and the name has to do with the way plastic responds to heat. These materials become liquid at their melting point, and a major attribute about thermoplastics is that they can be heated to their melting point, cooled and reheated again without significant degradation. Instead of burning, thermoplastics liquefy, which allows them to be easily injection moulded (Mechanisms, 2015). This is to introduce the next step over the sample preparation.

Since the material after being removed from the mixer is hard to manipulate, an efficient strategy for continuation of the sampling process was essential. To serve these ends, enough material was extracted from the mixer for 18 different percentages of case studies. Since the cylinder cavity is relatively small, the extracted materials cannot fit in directly. In this way, and with the cooperation of the Materials department, it was decided to use liquid nitrogen (at a temperature of -180°C , fig.34).



Figure 34 - Liquid nitrogen

In this way, it was possible with the help of a hammer to quickly shred into pieces all the material extracted from the mixer. This allowed to save crucial time to the entire experiment, since the alternative solution was to use a laboratory scissor instead fig. (35;36;37).

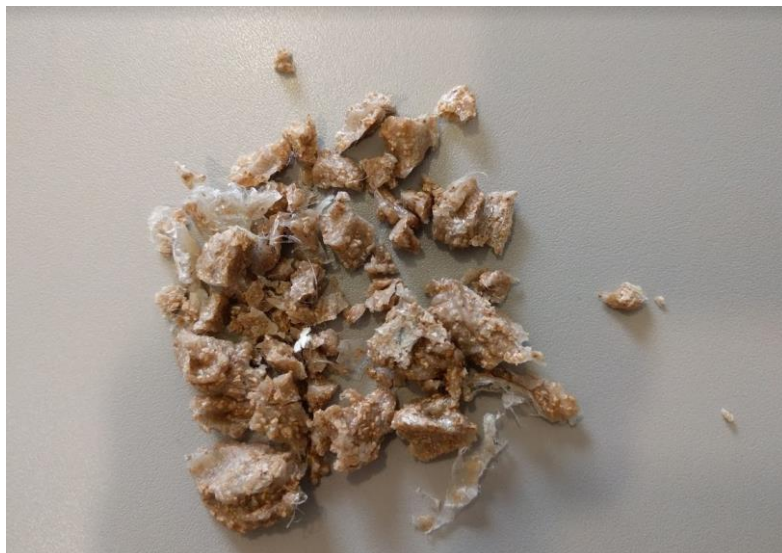


Figure 35 - Shredded PE composite



Figure 36 - Shredded ABS composite



Figure 37 - Different shredded CPC's

After this step of the process solved and accomplished, is time to enter the last phase of the experiment. The injection moulding machine used in this process is relatively simple and easy to manoeuvre, as you can see an image of it in fig.38.



Figure 38 - Injection moulding machine

The machine components can be divided into three main segments: cylinder (fig.39), piston (fig.40) and mould (fig.41). The following procedure is followed for all the sample injections:

1. Insert the raw material into the cylinder (3/4 of the cylinder volume, enough material to build one sample);

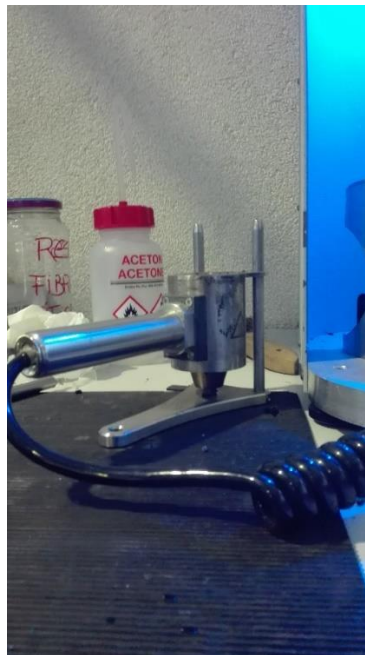


Figure 39 - Injection moulding cylinder

2. Press the compactor over the material in the cylinder, in order to avoid temperature differences to the outside and to avoid the material erupting outside the cylinder (due to the heat, material expands);
3. Let the material rest inside the cylinder for an average of 5 minutes;
4. Inject the material, the piston will move down towards the cylinder and push the piston down. This will fill the mould with the material. It is important to refer that the injection process is divided into two stages: Injection and compaction. The injection pressure is around 7 bar (maximum that the university grid allows) and the compression pressure is 6 bar. This is the part of the injection process that is performed at a lower pressure and has the purpose of compacting the piece to avoid its contraction, besides avoiding other defects like piece break or poor formation;

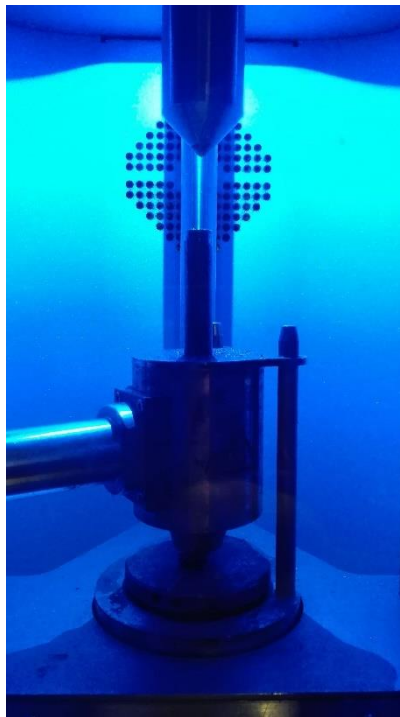


Figure 40 – Piston, compactor, cylinder and mould inside the housing

5. After the injection, it is time to take the mould from the cavity where it was inserted. A bucket of cold water is prepared to receive the mould, and let the material solidify for approximately 30 or 40 s;
6. After the last step, it is time to open the mould and visualize the sample;
7. Repeat the process for all the samples.

The entire injection process is now explained, it is time to understand the parameters and considerations taken during this step.

ABS samples were the first ones to be injected and the decision was to start from the pure polymeric material (100% ABS) downwards. This is due to the fact that since it is possessed the

technical file of the polymer, it helped to set up the initial parameters over the injector. Therefore, adding cork to the mixture will add some uncertainties to the process since the injection machine is normally used only with polymers.

According to the technical file, the processing temperature of ABS should be between 200°C and 220°C. The chosen temperature was 220°C, this is because the cylinder is not well insulated and has severe temperature differences across the entire body. Selecting a grade of 220°C ensured that all the material throughout the cylinder would reach the minimal temperature. Specifically, to prevent the front part (nozzle) from heating to a lower temperature than required, this was the precaution taken. The specified mould temperature for ABS injection is between 40°C to 70°C, and the procedure followed was the same as before. The chosen temperature is then 70°C.

The process went without major incidences till the samples of 40/50% of ABS. In both cases, the injection machine was unable to proceed with the experiment, based on the initial parametrization. The first thought was to raise the mould temperature to 80°C, since the injection pressure is fixed. This attempt was to reduce the temperature difference gap between the mould and the cylinder to evaluate if the injection problem was due to the fast solidification of the material during the process. However, the problem wasn't fixed and the doubts pursued. After discussing ideas with colleagues, it was possible to understand the origin of the problem relating to the non-injection on the highest percentages of cork over the CPC. The problem was related to the material solidification, but from a different root cause. The cylinder nozzle is in direct contact with ambient air, and despite the temperature inside the cylinder chamber slightly change from the rear to the front end, the nozzle extremity suffers from a temperature decrease, creating a layer of solid material working as a stopper. Whilst in samples with lower cork concentration this did not happen and it began to happen at a higher proclivity when there were increasing grades of cork applied to the mixture. The problem is uniquely because the mixture starts to lose the fluidity given by the polymer, that liquefies while cork does not transform at the same temperature/rate. The poor connection between cork grains and the liquefied polymer in higher concentrations, allows air to insufflate the mixture and create this layer on the nozzle. After solving this issue, the rest of the ABS samples were made with no more occurrences but both of them revealing a structural fragility visible to the naked eye.

Summarizing, the previous experiment and understanding gained through the obstacles faced allowed to become more prepared for the next steps of the laboratory work. It also raised some questions of how beneficial it is to add cork in higher levels such as 40% of the mixture and above. The samples notoriously start to suffer some degradation due to the excess of cork, and that is perfectly visible on fig.41.



Figure 41 - Mould open with 50% ABS

Since it is not possible to find data to compare the exact processes used, and the diversity of CPCs studied, a possible explanation to it is the lack of a binder to hold the connections between the polymer and cork in higher rates. The diverse substances did not mix into a homogenous substance and there was visible granularity identifiable between the cork and other polymer substance.

Proceeding with PC, the methodology was exactly the same as the one employed for ABS. Starting from the sample with 100% PC (fig.42) and going down in polymer percentage.



Figure 42 - PC specimen

Normally PC has higher melting temperatures when compared to ABS and PE, but since it was not possible to access the technical data of this exact type of PC, the decision was to start the injection with 250°C on the cylinder and the same 80°C mould temperature. The first attempt on these conditions was not successful, the mixture started to get out of the cavity because it was not liquefied enough to enter into the mould. The next step was to raise both temperatures to 280°C and 110°C, and for the pure PC sample the injection was effective. These mould temperatures were inside the data range collected from literature (Plastikcity, 2016), which for average PC pellets the mould working conditions should be between 85-120 °C and for the processing temperatures the interval range is between 280-320°C. For the pure PC samples and 90% CPC the injection occurred with no further incidents, but for the rest of the samples the same did not occur. The interface bonding is an important topic because for the remaining samples this did not happen, which indicates that some superficial modification or added coupling agents is needed (Fernandes, et al., 2010). After raising temperatures of the cylinder and mould, to a maximum of 300°C and 120°C respectively, it was still not possible to inject the rest of the samples.

Resuming, for the CPC with PC matrix, it was only possible to build two of the 7 initially proposed. This is the first drawback, but also allowed to understand that experimental work is full of uncertainties but at the same time very rewarding because scientific work is being accomplished.

PE matrix CPC, are the last ones to be processed. HDPE is known for its large strength-to-density ratio. The density of HDPE can range from 0.91 to 0.97 g/cm³. Although the density of HDPE is only marginally higher than that of low-density polyethylene, HDPE has little branching, giving

it stronger intermolecular forces and tensile strength than LDPE. The difference in strength exceeds the difference in density, giving HDPE a higher specific strength (Makeitfrom, 2011).

The same methodology as described above was followed and the initial conditions were 190°C for the cylinder temperature and 60°C for the mould temperature. The settings decision was obtained from colleagues past experiences with this material. Due to the fact of PE being more ductile comparing to PC and ABS, it is expected to reach the initial proposal of building samples till 60% of the CPC is cork basis. The injection was indeed smoother than when compared to CPC with PC matrix, till the highest cork percentage. In this case, it was necessary to change the work conditions initially to 210°C of cylinder temperature and in a second round to 230°C. At this point, it was possible to fulfil the objectives, despite the fact the bonding between cork and PE seems not to be stable due to the higher amount of cork. As a final remark on the last injection sample, it was visible some signs of burr along the sample. This is mainly because the pressure of injection was slightly above the desired, but even after the all the samples produced obtaining a perfect ratio between temperature and pressure is difficult to achieve. An example of the burr signs is observable on fig 43.



Figure 43 - Burred specimen

Resuming the sample production and comparing to the initial objectives, it is now possible to state that almost all objectives were accomplished. In the literature available, it was not found a single case of three CPC studied, with such a range of percentages for each case. Also, CPCs with 60% of cork were not found which makes an interesting case study.

In the next chapter, *Results and Discussion*, the two tests performed will be described (Charpy and Tensile test) and the results obtained from both. A discussion about the theoretical expectations vs actual results is also part of the chapter.

4. Results and discussion

4.1 Uniaxial quasi-static tensile tests

4.1.1 Methodology

In this set of tests, the objective is to evaluate three main mechanical properties:

- Young modulus (MPa);
- Ultimate tensile strength (MPa);
- Strain at ultimate tensile strength (%).

For the accomplishment of the tensile tests, no standards were followed because there is no specific standard for these types of composites. The quasi-static tensile tests were performed on the universal Shimadzu AG50KNG machine (fig.44) at a strain rate of $1,5 \times 10^{-3} \text{ s}^{-1}$, on at least 3 pieces of each type.



Figure 44 - Universal testing machine

The instrument used to obtain the measurements of displacement imposed on the specimen was a video extensometer Messphysik ME46NG (fig.45).



Figure 45 - Video extensometer

The video extensometer allows an individual to measure directly from the specimen; this was chosen because it is the most rigorous method.

Fig.44 shows a photograph of a specimen being tested with video extensometer. On the specimen, two marks are visible: a black circle impressed on white paper cut and pasted on it, which are continuously monitored by the video extensometer system, so that at the end of the performed test it will be collected a file with the cartesian coordinates of the two points, which in turn will give rise to the deformation values in function of time. Also, in the same file, it is possible to see the load over time. It is then necessary to cross the data, load and coordinates in time to obtain the stress-strain curve. This is a relatively simple process to obtain, since a template on excel was created during this experiment to insert the data given by the machine. In this template are synthetized the equation needed to get the stress-strain curves from the input received by the machine. Initially, the test pieces were measured to determine their true size with the aid of a precision caliper ± 0.05 mm. All tests were carried out by means of visual inspection on the correct positioning of the test pieces in the centre of the support base, as well as the parallelism between the support base and the moving part. To calculate the stress and strain of the different specimens, the formulas used were the engineering (conventional) ones, as can be seen below:

$$\sigma = \frac{P}{A_0} \quad (1)$$

Where P corresponds to the increasing load, and A_0 is the cross-sectional area of the specimen. For the conventional strain, the formula is reached by dividing each increment ΔL of the distance between the gage marks, by the corresponding value of L , the elementary strain is obtained:

$$\Delta \varepsilon = \frac{\Delta L}{L} \quad (2)$$

From these two formulas, it is now possible to extract valuable information in order to compare all the samples tested. For each specimen, stress-strain curves were created and from the actual figures that compose the data charts it is obtainable the following:

- Young Modulus [MPa], calculated from strain 0.05 to 0.25%
- UTS [MPa]
- Strain at UTS [%]
- Elongation [%], only for ABS CPCs (data was not collected for PC and PE samples)

For each sample, information from three specimens is collected and displayed in a table, as can be seen in the following example (table 3).

Table 3 - Example of data collection and analysis

Young Modulus		Specimen 1	Specimen 2	Specimen 3
	MPa	1504,4	1838,6	1883,9
		MEAN	1742,3	
UTS		Specimen 1	Specimen 2	Specimen 3
	MPa	37,5	39,6	38,7
		MEAN	38,6	
Strain at UTS		Specimen 1	Specimen 2	Specimen 3
		0,04	0,03	0,03
	%	4,0%	3,4%	3,1%
		MEAN	0,04	3,5%
Elongation at break		Specimen 1	Specimen 2	Specimen 3
		0,14	0,07	0,14
	%	14,2%	6,7%	14,1%
		MEAN	0,12	11,7%

The objective is to compare the information from all the CPCs, and in order to have a visual comparison of the stress-strain curves of all the samples a polynomial trendline approximation was used, as can be seen in the graphic below (fig.46). Since the degree of certainty was considerably high, it was used 2nd order polynomial equation.

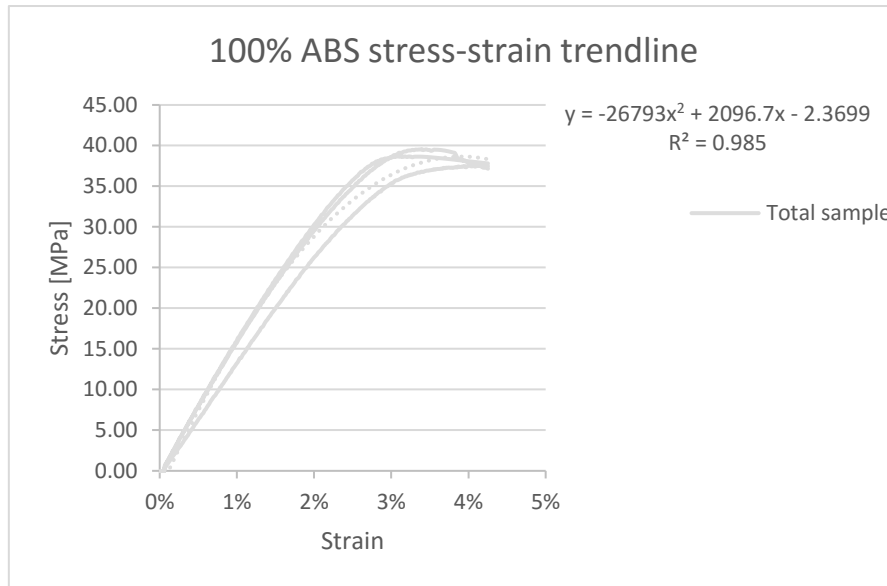


Figure 46 - Polynomial equation of the three specimens

In the next chapter, *4.1.2 Results*, all the results from the tensile tests are displayed, and the necessary comparisons are made to comprehend the results obtained.

4.1.2 Results

In the fig.48, it is possible to observe the curves obtained from the tensile tests. It is immediately perceived the difference in mechanical characteristics to deformation for each one of the polymers, independent of the cork added. Polycarbonate as expected is the most mechanically resistant, followed by ABS and at last PE. The purpose of this figure is to, first, get an understanding of the polymer characteristics, such as the fragile behaviour to forces of the PE but high elasticity, and the high rigidity of ABS and PC since the curve slope is much more pronounced. Second, to evaluate briefly what happened when cork was added, and as expected, the mechanical resistance to traction is inferior. Nevertheless, the results are extremely positive and highlight several very important takeaways. It is observable in the presentation of the resulting data from this study that there is minimal difference in the samples on the ABS in a range of cork augmentation reaching as high as 30%. These results are interesting and it also needs to be noted that for the PE there is almost no discernible change in mechanical properties. This means the process of mixing and injection was well achieved, because otherwise the results would not have delivered the quality or resistance observed during this study.

The visual analysis of the test specimens used in the tensile tests allowed it to be observed that all fractures occurred in the upper part of these (fig.47), but still in the region which is given the useful length name.

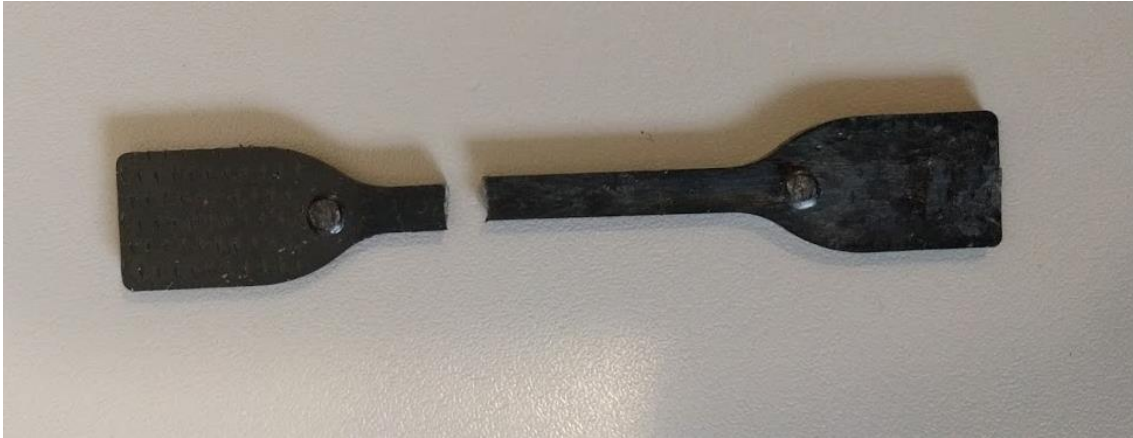


Figure 47 - Fracture of the specimen

This fact can be explained by prior treatment of the samples, which occasionally generates stress accumulation in regions where there are failures, which in turn, are related to injection problems such as mould temperature, injection pressure and other variables that must be properly selected for the success of the moulding.

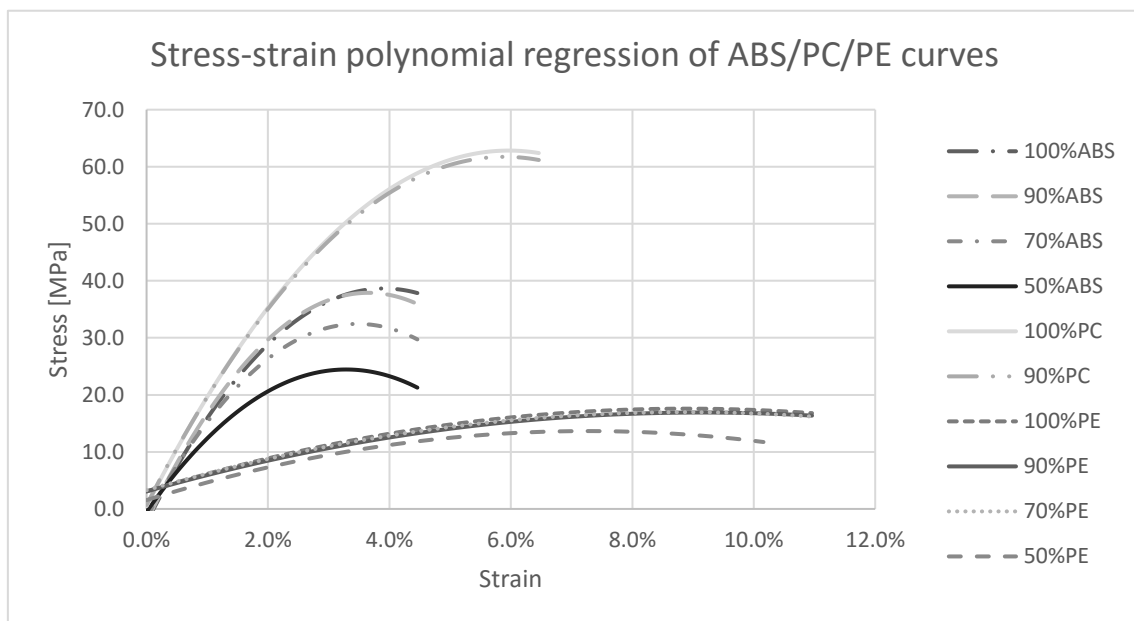


Figure 48 - Stress-strain polynomial regression of ABS/PC/PE curves

Stress-strain curve is presented in fig.48 while at table 4 are represented the main relevant points extracted from the tensile testing. Young Modulus is the ratio of stress to elastic strain in tension. A high Young Modulus means that the material is rigid - more stress is required to produce a given amount of strain and resulting elongation of the material. Tensile strength is the capacity of a material or structure to withstand loads tending to elongate. In other words, tensile strength resists tension (being pulled apart). The strain on tensile strength, as the phrase indicates, is the value of the strain in percentage on the point of maximum strength. Elongation at break, also

known as fracture strain, is the ratio between changed length and initial length after breakage of the test specimen. It expresses the capability of a material to resist changes of shape without crack formation.

Regarding the results displayed in the table, starting by elasticity, the discussion needs to be focused on two directions, the absolute values of the results and the tendencies due to cork addition. Elasticity is directly correlated to the stiffness of the material. Since polyethylene is more elastic and ductile, it is supposed to have the lowest values for young modulus. This means, that it will be in the elastic region more time and have lower dimensional stability. In terms of Polycarbonate and ABS, the values are significantly higher and that was predicted, due the materials stiffness. Cork properties are not an advantage on tensile tests, since its low resistance to traction. However, this research is important to understand what happens to the different composites when cork is added, and also to realize on how the quantity of cork added changes the materials characteristics.

Specimen ID	Young Modulus (MPa)	Ultimate tensile strength (MPa)	Strain on maximum tensile strength (%)	Elongation at break (%)
ABS 100%	1742,30	38,60	3,50%	11,67%
ABS 90%	1750,99	38,11	3,19%	8,06%
ABS 70%	1556,51	32,17	3,09%	4,64%
ABS 50%	1487,84	23,80	3,00%	4,55%
Specimen ID	Young Modulus (MPa)	Ultimate tensile strength (MPa)	Strain on maximum tensile strength (%)	
PC 100%	2105,99	62,43	6,06%	
PC 90%	2108,92	61,23	5,97%	
Specimen ID	Young Modulus (MPa)	Ultimate tensile strength (MPa)	Strain on maximum tensile strength (%)	
PE 100%	1084,48	17,20	11,60%	
PE 90%	1054,76	16,48	11,59%	
PE 70%	1053,40	16,42	10,92%	
PE 50%	974,65	13,30	8,83%	

Table 4 - Results from the tensile testing

In the tensile strength parameter, the results also match the expectations. Starting from the polymer characteristics, PC is known by its strength, dimensional stability, heat distortion temperature and impact resistance of the blends which is confirmed by the results presented. Regarding ABS, it is not as strong as ABS (its main properties are processing advantages, chemical resistance besides cost reduction with respect to PC) but achieved results inside the expectations (Ping L, 1998). PE as expected, is the less resistant of the three, presenting lower

values in this parameter. Elasticity and Tensile strength are directly proportional, which means for higher elasticity values the tensile strength will be superior as well. The addition of cork will decrease the tensile strength of the samples, because it will disrupt the bonds of the polymer itself and this creates instability towards the specimen (due to cork characteristics, mixing process, lack of adding binder, etc.).

Strain on maximum tensile strength is one characteristic related to the two explained before, which can be explained by the material stiffness. However, in this case, it is inversely proportional (higher material stiffness lower maximum strain).

Elongation was only measured on ABS (only material that was traction till fracture) and the results couldn't be more elucidative regarding the cork interference. Since cork does not liquefy at the temperatures tested, the bonding between cork and polymer is not as strong and due to the cork characteristics referred above, this cause the reduction on elongation when raised the cork percentage over the specimen.

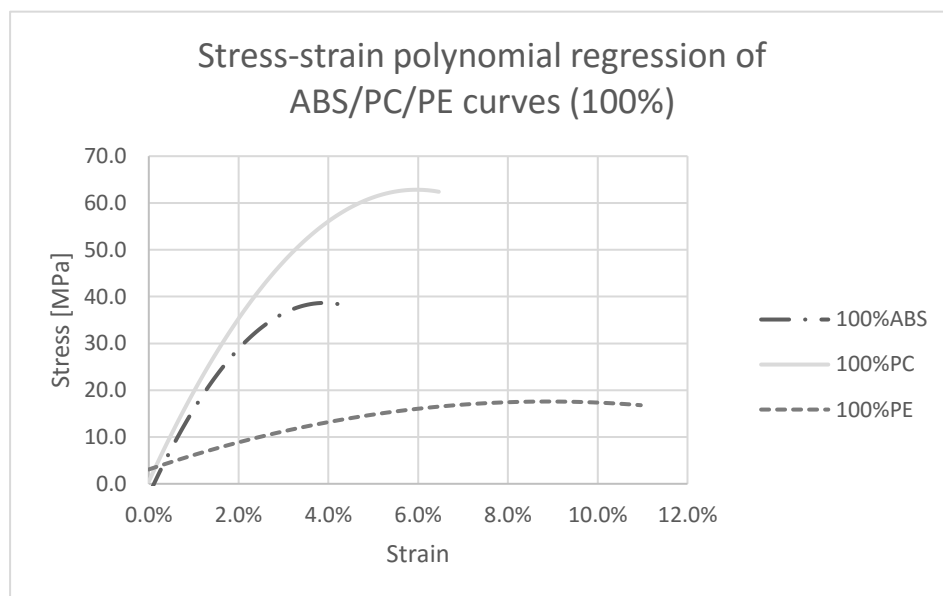


Figure 49 - Stress-strain polynomial regression of ABS/PC/PE curves (100%)

This figure reflects the stress-strain curves of the polymers, with no cork added. The objective of it is to show how different are the behaviour lines and give a fair comparison between the three.

The overall results from tensile studies confirmed that PC has superior properties in all three aspects that is stiffness, strength and ductility over ABS (Hassan & Yean Jwu, 2005). As expected, the mechanical properties of PE are inferior when compared to the above polymers, but on the other hand the elongation is highly superior.

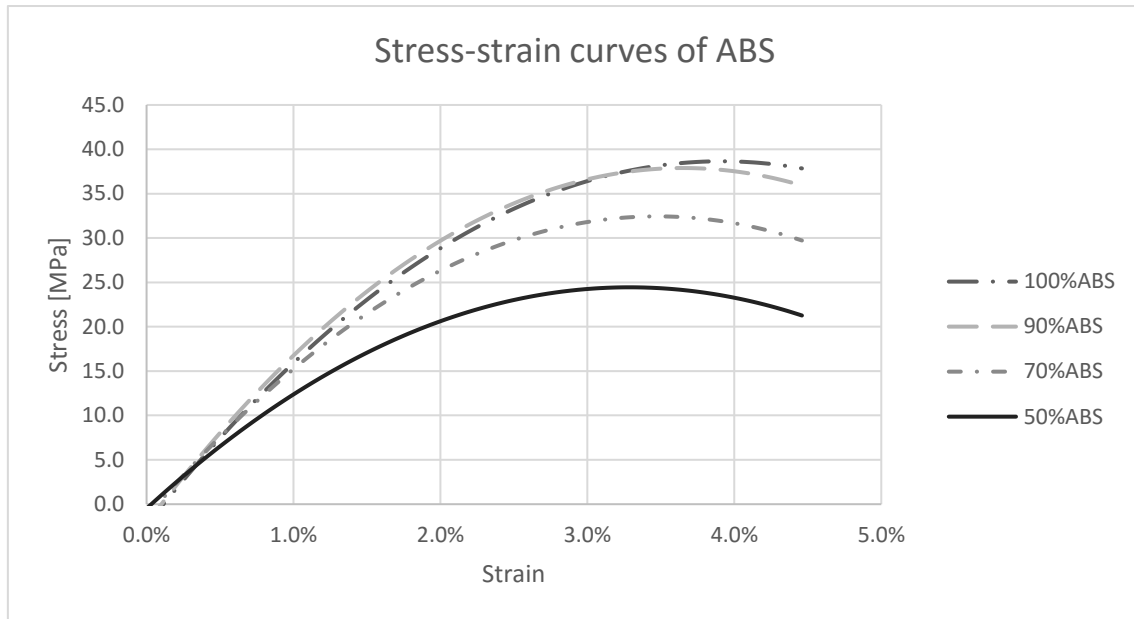


Figure 50 - Stress-strain curves of ABS

Regarding ABS composites, in this case, the analysis will start from the lowest results and progress upwards from there. In *chapter 3.2* (Sample Production, pag.36), it was referred the complexity of the injection on high cork levels (50 wt.%), revealing poor structural bonding between polymer and cork, is notorious on fig. 50 & 51 the link to it. The resulting reduction on tensile strength (20%) when compared to ABS (70 wt.%) and the lack of elongation when compared to the above is significant. The diminished percentage of elongation indicates a better dimensional stability, which means a smaller variation on the total length till the moment of fracture. Despite the fact that the elongation on both sides is nearly identical, the results achieved by ABS (70 wt.%) are significantly better. As it can be seen in fig.51, this sample achieved small losses in strength, around 15%, which in the case of ABS (50 wt.%) was over 35%. The probable cause of this difference can be justified by the manufacturing process; due to the absence of a binder for high percentages of cork, the specimens don't establish the stability needed. A subsequent study to this could be conducted in such a manner to compensate for this inadequacy to improve the performance of the substance as it because higher percentage of cork to establish elevated levels of stability to create a more comparative analysis of the varying substances. In terms of ratio between cork usage and mechanical properties, the results obtained for the ABS (70 wt.%) are the most interesting ones, since it was outstanding being able to insert this quantity of cork without the use of additives and obtain these results. For the ABS (90 wt.%), the outcome is highly positive as well. In terms of elasticity, the values were slightly higher when compared to ABS (100 wt.%), and in terms of strength at tensile the decrease was only about 5%.

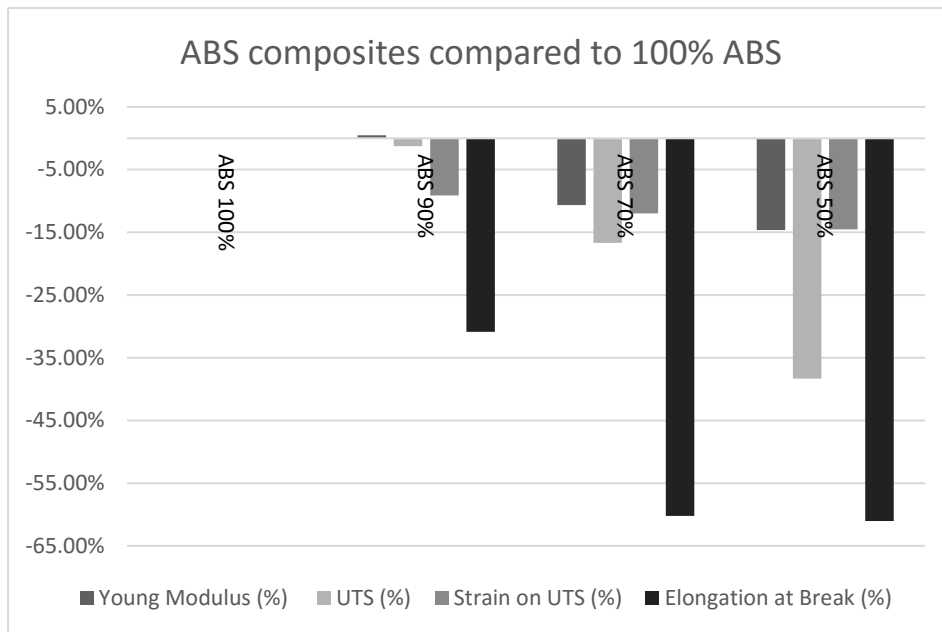


Figure 51 - ABS composites compared to 100% ABS

Regarding Polycarbonate tensile testing, even though as cited before it was only possible to inject PC (100 wt.%) and PC (90 wt.%) due to difficulties in the injection parameters, the results were the most satisfying due to the inherent mechanical properties of PC. This is the strongest polymer of the three, with the desired characteristics considering the aim of the testing.

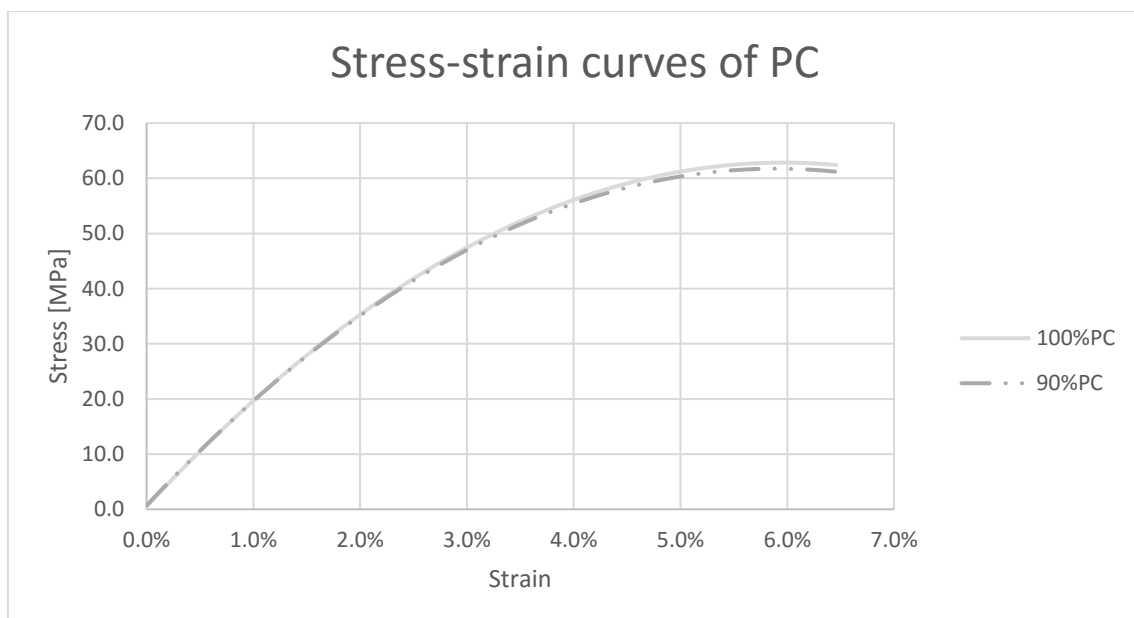


Figure 52 - Stress-strain curves of PC

For both samples, the results were so similar. This comparability can be indicative for the good preparation of the raw material and consequent injection. These specimens reached a stress peak

around 62 MPa, a Young Modulus of 2100 MPa (ABS (90 wt.%) got even a residual gain on this characteristic) and a strain at peak of 6%. This means that even though PC is stiffer than ABS, it also shows a better flexibility.

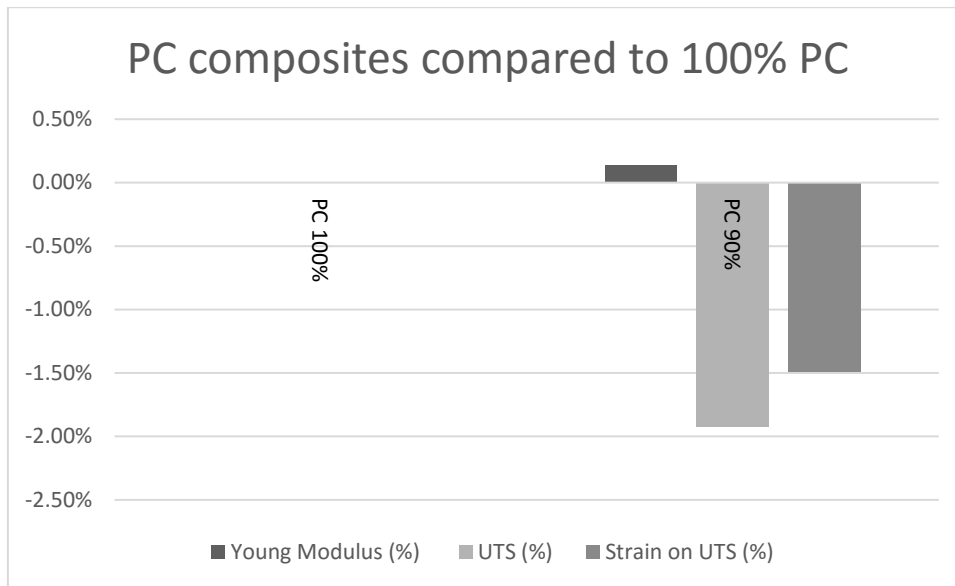


Figure 53 - PC composites compared to 100% PC

(Shimadzu, 2017), made some tests with plastics as it can be seen in fig. (54). They have used a 1 mm/min load speed (against the 3 mm/min in this experiment), but it is an evidence that the results obtained have credibility and scientific value. Directly comparing the results of PC (100 wt.%) with the PC from Shimadzu testing, it is very easy to understand the resemblance. Regarding Young Modulus, our sample showed a value of 2106 MPa approximately, and from Shimadzu the value is 2410 MPa (13% difference). The tensile strength of Shimadzu PC sample is 64.9 MPa against 62.4 MPa (4% difference). The strain at maximum tensile strength, in this dissertation, is 6.06% versus the 5.97% (0,09% difference). In this case, elongation was not evaluated so it is not possible to compare with the Shimadzu testing.

Specimen ID	Elasticity (MPa) Calculated from strain 0.05 to 0.25%	Tensile Strength (MPa)	Strain with respect to values at left (%)	Elongation at Break (%)
PE	1460	29.9	6.93	56.5
PP	1940	38.2	6.84	28.4
PVC	3240	66.6	3.43	8.75
PC	2410	64.9	5.97	82.7

Figure 54 - Shimadzu polymer testing results (Shimadzu, 2017)

From these results, it is evident and a proof of confidence towards the methodology implemented, because in laboratory work it is difficult to have terms of comparison due to the differences on methodologies used.

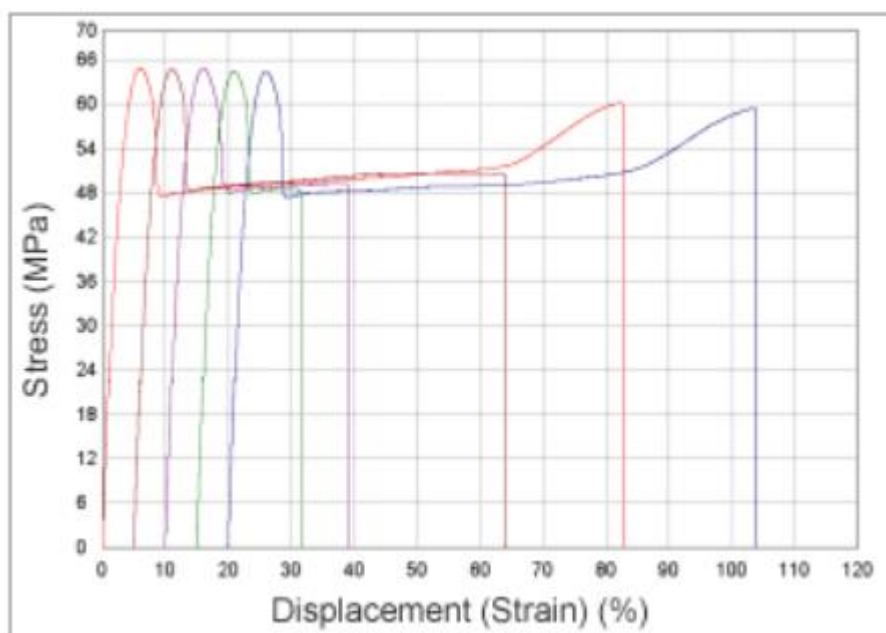


Figure 55 - Stress-strain curves of Shimadzu results on PC

The stress-strain curves of PE are not the most attractive in terms of strength, even though it is a HDPE (one of the more resistant classes of PE), it has scientific interest. Starting from the small curve variation until PE (70 wt.%), which is nearly the same as the PE (100 wt.%). The meaning of these results, it is probably due to the fact of PE possessing a low MSI (Melt flow Index), which is highly useful in the injection process, because it indicates the level of fluidity from the plastic. This turned to be, as it seems, an advantage towards the specimen's equilibrium and homogeneity. Since this plastic is not used in same range of applications as ABS or PC, since it shows a more ductile behaviour when compared to the rest, the maximum strength only reached the peak of less than 18 MPa, At the same time, it stays in the elastic region longer, presenting no dimensional stability since the beginning of the testing. Due to the speed of testing, it was not possible to evaluate the elongation because PE can be stretched for long periods of time when bound to small strain rates. The sample PE (50 wt.%), as it happened in ABS, exhibited signs of saturation due to the amount of cork. The polymer cannot bond as well, and that is notorious on the results achieved, with an interesting difference when compared to the other samples.

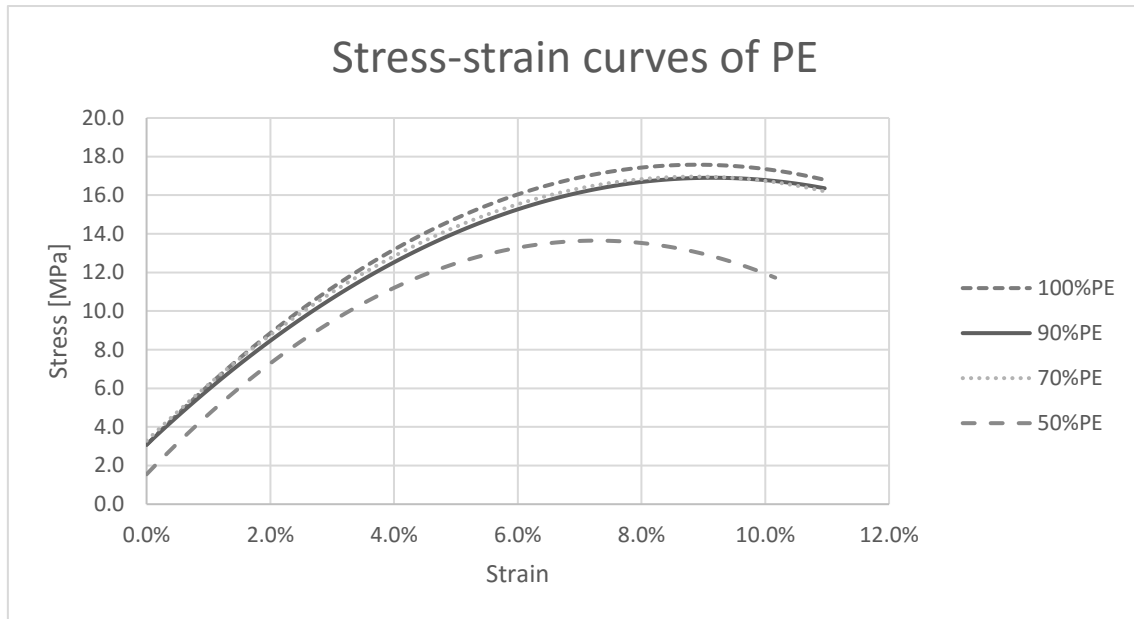


Figure 56 - Stress-strain curves of PE

As reviewed above, the results of the first three samples are highly comparable. The differences in all the characteristics are lower than 5%, when compared to PE (100 wt.%). On PE (50 wt.%) these differences are approximately 10% for Young Modulus loss, nearly 22% for reduced tensile strength and less 23% on strain at the maximum point.

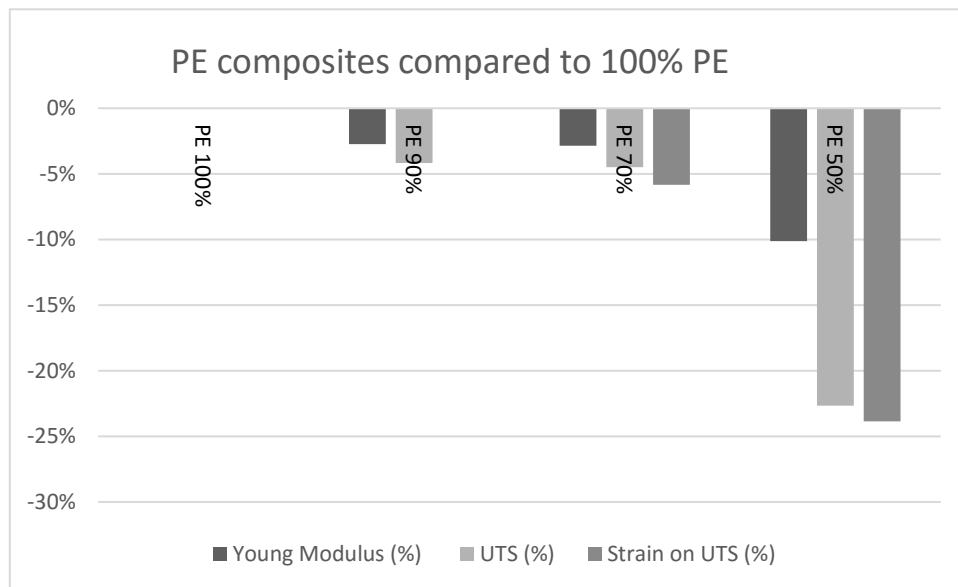


Figure 57 - PE composites compared to 100% PE

In the next sub-chapter, the *Charpy Test* will be explained how it is developed this kind of test and with which purpose, and after that, the explanation of the results achieved.

4.2 Charpy test

4.2.1 Methodology

The next stage of this dissertation is to evaluate the tenacity of the composites tested. To this end, the usage of a laboratory in ESAN (Escola Superior Aveiro Norte) was requested, a complex owned by the University of Aveiro, which kindly accepted and allowed the research to be conducted in their facility.



Figure 58 - ESAN

The Charpy test can be used for different purposes. In this case, it was employed evaluate the tenacity of the materials, (tenacity is the quantity of energy that a material can take before it fractures, as an example, ceramic materials have a low tenacity) since the main objective is to understand the composite behaviour for the helmet outer shell application. Also, to understand the influence of cork on augmenting or diminishing the polymers tenacity. Charpy tests can also be used for resilience studies, which is the material characteristic to accumulate energy when subjected to stress, without having fracture.

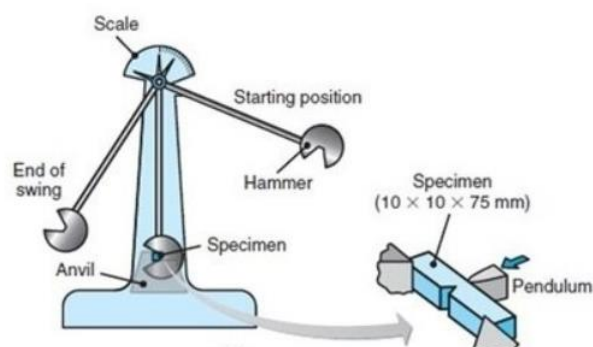


Figure 59 - Charpy test, (Quora, s.d.)

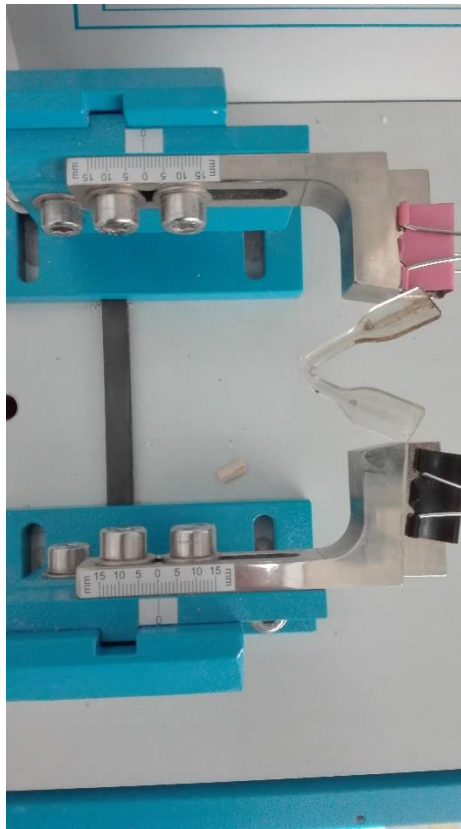


Figure 60 - Specimen being tested

The apparatus consists of a pendulum of known mass and length which is withdrawn from a known height, impacting the material to be tested. The energy transferred to the material can be measured by comparing the difference in hammer height before and after fracture (energy absorbed by the fracture event).

The methodology for this testing is relatively simple to implement. The experiment basis is the testing of 3 specimens for each sample, make an average of the energy absorbed and display it as a graphic of bars. In this test the type of fracture is not studied, due to time restrictions.

In table 5 are the known parameters for the conduction of the experiment. The energy of impact is calculated using the kinetical energy equation, since the velocity on the time of impact is known.

Table 5 - Initial considerations on charpy testing

Type of test	Charpy	Energy of impact (KJ)	3,998955
Distance between supports (mm)	40	Resistant area (mm²)	8
Velocity (m/s)	2.9	Pendulum mass (Kg)	0.951

4.2.2 Results

The results of the Charpy test are displayed below. These results are interesting to discuss, because if in the tensile testing it was visible a major difference in terms of strength between PE and the other two polymers, in this case PE showed a major improve on results. In the pure polymer samples (100 wt.%), PC was able to absorb nearly 50% of the impact, ABS approximately 40% and PE almost 30%. This indicates that PC is the most tenacious polymer of the three, and with the addition of cork the results tend to decrease. This is due to the fact that cork is highly resilient but not very tenacious. That is why it is interesting to evaluate how this addition would affect the general results.

In the second sample (90 wt.%), the results demonstrate what was explained above. The energy absorption by PC and ABS decreased 20%, and by the PE only 10%. This means, that with only 10% of cork in the mixture, ABS and PE have the same energy absorption capability. The justification of this phenomena, can be related to two things: The injection process, because due to the low MSI this was the easiest material to inject and avoid some surface tensions, allowing to be in the best conditions for testing. Also, the intrinsic material characteristics of PE, that even though in the tensile testing doesn't reveal the same strength as ABS, in this case the characteristics needed for a good performance are completely different. The fact of being not as stiff as ABS might help in the tenacity performance.

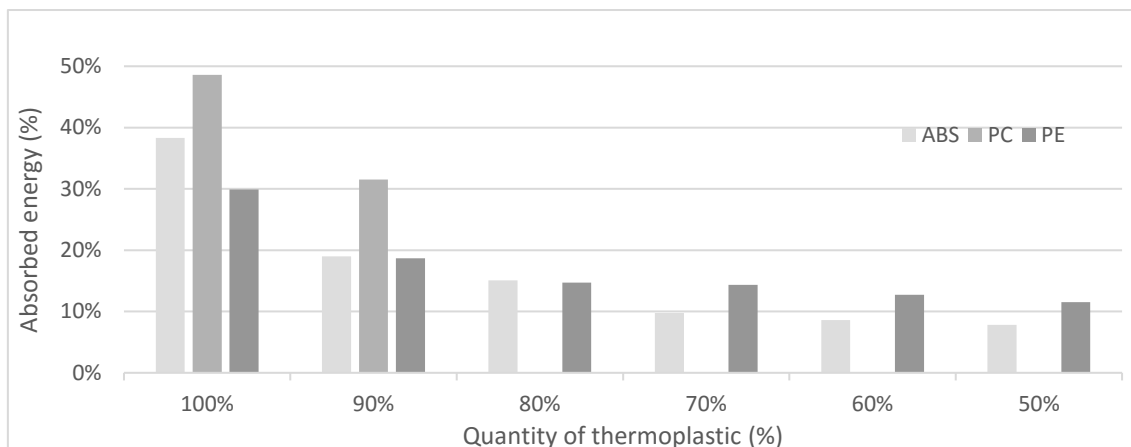


Figure 61 - Charpy results

In the remain samples, the energy absorption variation was not as big when comparing to the initial ones. PE maintained a stable energy absorption around 15%, while ABS started to decrease slowly till the minimum of 8%.

Resuming, PC once again revealed to be the best candidate in terms of mechanical properties, being almost flawless in all the characteristics studied. ABS showed poor tenacity, which for the application in question is not favourable, indicating that this CPC probably would need a different treatment or some binder addition, while PE showed relatively good results.

5. Conclusions

5.1 Achieved goals

The work developed throughout this Dissertation allowed to establish guidelines on the CPCs processing and testing. The value of cork is huge, being recognized widely for the diversity of applications used and the excellent properties of this natural material. In this work, it was used cork powder (or cork grains), normally seen by companies as a surplus, once for the main cork applications it cannot be used. Being able to process a material that normally is considered waste, and try to implement it with polymers is highly stimulating for two reasons: finding a new way to use a disposable material and at the same time, try to implement a green material on applications than normally only use polymers and becoming more biodegradable than before. This was achieved during this Dissertation, once it was possible to produce samples with 50% of cork in it. This was achieved without the use of any kind of adherent, and in the literature consulted it is extremely hard to achieve, in such high percentages of cork. The entire samples manufacturing process was extremely challenging due to the different polymer properties, and by the fact of not being able to find in literature such a wide study to understand if the direction followed was the correct or if the results achieved were inside the predictions. All the steps of the process, such as the choice of the mixing properties (temperature, torque of the machine), the injection process (temperature of the mould, temperature of the cylinder, injection pressure and compacting pressure) or the drawbacks existed on the injection of certain samples, count as an achieved goal since all the knowledge took from this was not possible without all the try's and errors. The initial objective of having 60% of cork in all the samples was not concretized, but all the process of writing a dissertation is evolutionary, and the initial expectations were not viable because of the existing constraints (i.e. injection pressure of the lab equipment).

It was already known from the beginning that the testing that was about to be performed, it would not benefit the cork properties (tensile and Charpy test). Nevertheless, the interesting part of it is to try to reach a ratio of cork usage that allows these CPCs to be used on several applications (not only helmet outer shell). In the tensile testing, the results achieved by ABS (70 wt. %) is fairly interesting, since 30% of cork in a specimen is relatively high, and this would be helpful to reduce considerably the average weight of the samples while avoiding a relatively large loss on mechanical properties. In the Charpy test, the polymer with the best average results was PE, that was able to maintain a constant energy absorption of nearly 15% till PE (50 wt%).

Resuming, despite the material that revealed the best performance was PC, it is fair to say that if the CPC are able to maintain some of the original plastic properties, the addition of cork will introduce new features like acoustic and thermal insulation, which will be benefit CPC range of properties.

5.2 Future work

Writing a Dissertation is an evolutionary process and during this period several ideas start to come over as your knowledge on the subject also develops. As future works, it would be interesting to evaluate the incorporation of a binder in the samples, because with high amounts of cork it was difficult to obtain solid specimens, and with the help of a binder, quantities also should be studied, it would make the testing more feasible.

In the processing of the CPCs, evaluate how different pressures, different mixing torque or different temperatures change the material behaviour while testing, as well as the surface characteristics of the specimens.

At last, the addition of a compression test to the samples it would interesting, since it would benefit cork properties and understand the behaviour of the CPCs at yield and at fracture.

6. References

Aare, M., 2003. *Prevention of head injuries focusing specifically on oblique impacts*, Stockholm, Sweden: School of Technology and Health, Royal Institute of Technology.

Amorim, 2017. *Corticeira Amorim*. [Online]

Available at:

https://www.amorimcork.com/media/filer_public_thumbnails/filer_public/2012/12/12/rolha-amorim_1.png_327x311_q95.png

[Accessed in 15 10 2017].

Amorim, C., 2017. *Cork and Applications*. [Online]

Available at: <https://www.amorimcork.com/pt/natural-cork/cork-and-other-applications/>

[Accessed in 29 10 2017].

Antiques, P. M., 2012. *P&K Military Antiques*. [Online]

Available at: <http://www.pandkmilitaryantiques.co>

[Accessed in 03 03 2017].

APCOR, 2016. *APCOR - Montado e floresta*. [Online]

Available at: <http://www.apcor.pt/montado/floresta/>

[Accessed in 26 10 2017].

Array, C., 2017. *ABS helmet*. [Online]

Available at: http://www.chinaarray.com/images/polymers/abs_helmet.jpg

[Accessed in 15 10 2017].

Associação Portuguesa da Cortiça, 2009. [Online].

Beusenberg, M. C. & Happee, R., 1993. *An experimental evaluation of crash helmet design and effectiveness in standard impact tests*. Eindhoven, Netherlands, s.n.

BorgWarner Chemicals, 2015. *ABS (Acrylonitrile-Butadiene-Styrene) Resins*, Washington: BorgWarner Chemicals.

Bosch, H. L. A. v. d., 2006. *Crash Helmet Testing and Designs Specifications*, s.l.: s.n.

- Cernicchi, A., Galvanetto, U. & Iannucci, L., 2008. Virtual modelling of safety helmets: practical problems. *International Journal of Crashworthiness* 13 (4), pp. 451-467.
- Deck, C. & Willinger, R., 2006. Multi-directional optimisation against biomechanical criteria of a head-helmet coupling. *International Journal of Crashworthiness*, pp. 561-572.
- Division, U. N. S., 2016. *UN COMTRADE*. [Online]
Available at: <https://comtrade.un.org/db/ce/ceSnapshot.aspx?px=H2&cc=45>
[Accessed in 28 10 2017].
- Fernandes, E. M. et al., 2010. Cork based composites using polyolefin's as matrix: Morphology and mechanical performance. *Composites Science and Technology*, Volume 70, pp. 2310-2318.
- Fernandes, E. M. et al., 2011. *Properties of new cork-polymer composites: Advantages and drawbacks as compared with commercially available fireboard materials*, Guimarães: Elsevier.
- Fortes, M., 2004. A Cortiça. *IST Press*.
- Freedonia, 2013. *World Motorcycles*. [Online]
Available at: <https://www.freedoniagroup.com/industry-study/world-motorcycles-2972.htm>
[Accessed in 25 07 2017].
- Ghajari, M., 2009b. *Influence of the body on kinematic and tissue level head injury predictors in motorcyclists accidents*. York, UK, s.n., pp. 9-11.
- Gibson, L. J. & Ashby, M. F., 1997. Em: *Cellular Solids: Structure and properties*. 2nd ed. Cambridge: Cambridge University Press.
- Gibson, L. J. & Ashby, M. F., 1997. *Cellular Solids: Structure and properties*. 2nd ed. s.l.:Cambridge University Press.
- Gilchrist, A. & Mills, N. J., 1994a. *Impact deformation of ABS and GRP motorcycle helmet shells*. *Plastics Rubber and Composites Processing and Applications*. s.l.:s.n.

Gold, T. G., 2012. *The Greek gold*. [Online]

Available at: <http://www.greekgold.com/items/485/504.jpg>

[Accessed in 03 03 2017].

Gonçalves, D. F. d. S., 2009. *Simulação Numérica*, Aveiro: Universidade de Aveiro.

Halldin, P., Gilchrist, A. & Mills, N. J., 2001. A new oblique impact test for motorcycle helmets. *International journal of Crashworthiness*, pp. 53-64.

Hassan, A. & Yean Jwu, W., 2005. *Mechanical Properties of High Impact ABS/PC blends - Effect of Blend Ratio*. Ogos, SIMposium Polimer Kebangsaan .

Holbourn, A. H. S., 1945. The mechanics of brain injuries. Em: *British Medical Bulletin* 3. s.l.:s.n., pp. 147-149.

Hooke, R., 1665. *Micrographia or some physiological descriptions of minute bodies made by magnifying glasses*. 1st ed. s.l.:s.n.

Huang, S. C., 1999. Numerical simulation of human head-neck dynamics. *Bio-Medical Materials and Engineering*, pp. 66-71.

Hulme, A., Mills, N. J. & Gilchrist, A., 1995. *Industrial head injuries and the performance of the helmets*. Switzerland, s.n.

Jardin, R., 2015. *Caracterização do comportamento mecânico em regime estático e dinâmico de aglomerados de cortiça*, Aveiro: Universidade de Aveiro.

Kermezli, T., 2017. *Mechanical behaviour of cork modified by heat treatment at high temperature*, s.l.: Mechanika.

Kim, G. H., Lee, O. S. & Yoo, S. S., 1997. Experimental study on impact absorbing performance of motorcycle helmets. *KSME International Journal*, pp. 292-299.

Kostopoulos, V., Markopoulos, Y. P., Giannopoulos, G. & Vlachos, D. E., 2002. Crashworthiness study of composite motorcycle safety helmet. Em: *Composites Part B*. s.l.:s.n., pp. 99-107.

Makeitfrom, 2011. *Compare Materials: HDPE and LDPE*. [Online]

Available at: [Makeitfrom.com](http://www.makeitfrom.com)

[Accessed in 10 11 2017].

Matweb, 2017. *Materials properties*. [Online]

Available at: <http://www.matweb.com/>

[Accessed in 18 09 2017].

Mechanisms, C., 2015. *Creative Mechanisms*. [Online]

Available at: <https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-polycarbonate-pc>

[Accessed in 16 10 2017].

Mechanisms, C., 2017. *Everything You Need to Know About ABS Plastic*. [Online]

Available at: <https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-abs-plastic>

[Accessed in 15 10 2017].

Mechanisms, C., 2017. *Polycarbonate*. [Online]

Available at: <https://www.creativemechanisms.com/blog/everything-you-need-to-know-about-polycarbonate-pc>

[Accessed in 15 10 2017].

Mechanisms, C., 2017. *Polyethylene*. [Online]

Available at: <https://www.creativemechanisms.com/blog/polyethylene-pe-for-prototypes-3d-printing-and-cnc>

[Accessed in 15 10 2017].

Mills, N. J., 1993. *Plastics. Em: Microstructure and Engineering Application*. Paris: Arnold.

Mills, N. J., 1995. *Role of components of motorcycle helmets*, UK: s.n.

Mills, N. J. & Gilchrist, A., 1991. The effectiveness of foams in bicycle and motorcycle helmets. Em: *Accident Analysis and Prevention*. s.l.:s.n., pp. 153-163.

Mills, N. J. & Gilchrist, A., 1992. *Motorcycle helmet shell optimisation*. Portland, s.n., pp. 149-162.

Moda, 2017. *Moda... Moda....* [Online]

Available at: <https://modamodahp.files.wordpress.com/2011/07/moda-cortic3a7a1.jpg>

[Accessed in 15 10 2017].

N. Nemirovsky et al, 2010. *A new methodology for biofidelic head-neck postural control.*

Hanover, Germany, s.n., pp. 71-84.

Newman, J., 2005. *The biomechanics of head trauma and the development of the modern helmet. How far have we really come?*. Prague, s.n.

Pandey, M. M., 2017. *Applications of ABS plastic.* [Online]

Available at: <https://www.linkedin.com/pulse/applications-abs-plastic-material-madan-m-pandey/>

[Accessed in 15 10 2017].

Pereira, H., 2007. *Cork: biology, production and uses.* s.l.:Elsevier Science.

Ping L, K., 1998. Polystyrene and Styrene Copolymers: Their Manufacture and Application.

Em: *Advances in Polymer Technology.* s.l.:s.n., pp. 201-223.

Plastikcity, 2016. *Plastikcity.* [Online]

Available at: <https://www.plastikcity.co.uk/useful-stuff/material-melt-mould-temperatures>

[Accessed in 22 10 2016].

Quora, s.d. *Charpy test.* [Online]

Available at: <https://qph.ec.quoracdn.net/main-qimg-eda807289c0813fe85ecb487550db433-c>

Rice, T. M. et al., 2017. Novelty helmet use and motorcycle rider fatality. *Accident Analysis & Prevention*, Volume 103, pp. 123-128.

Richter, M., Otte, D. & Lehman, U., 2001. Head injury mechanisms in helmet-protected motorcyclists: prospective multicenter study. *Jornal of Trauma*, pp. 949-958.

Rosa, M. & Fortes, M., 1988. Temperature-induced alterations of the structure and. *Mater Sci Eng*, Issue 100, pp. 69-78.

Rosa, M. & Fortes, M., 1988. Thermogravimetric analysis of cork.. *J Mater Sci Lett*, pp. 7-10.

Roth, H. & Lombard, C., 1953. *Crash Helmet*. US, Patente N° 2,625,683.

Shimadzu, 2017. *Tensile Tests of Various Plastic Materials(1)*. [Online]

Available at: <https://www.shimadzu.com/an/industry/petrochemicalchemical/i215.html>

[Accessed in 15 10 2017].

Shuaib, F. M. et al., 2002b. Motorcycle Helmet: Part 2. Materials and design issues. *Journal of Materials Processing Technology* 123, pp. 422-431.

Shuaib, F. M., Hamouda, A. M. S., Radin Umar, R. S. & Megat Ahmed, M. M. H., 2007. A new motorcycle helmet liner material: the finite element simulation and design of experiment optimization. *Materials and Design*, pp. 182-185.

Study.com, 2017. *What is Polyethylene? - Properties & Uses*. [Online]

Available at: <http://study.com/academy/lesson/what-is-polyethylene-properties-uses-quiz.html>

[Accessed in 15 10 2017].

Tinard, V., Deck, C. & Willinger, R., 2012a. Modelling and validation of motorcyclist helmet with composite shell. *International Journal of Crashworthiness*, pp. 209-215.

TLVE, R., 2017. *Isolamento*. [Online]

Available at: <http://www.tlve-reabilitacoes.pt/wp-content/uploads/2015/08/isolamento-acustico.jpg>

[Accessed in 15 10 2017].

UTA, 2017. *Stress-strain*. [Online]

Available at: <http://web.uta.edu/faculty/ricard/Courses/KINE-3301/Notes/Images-14/Visco-Stress-Strain.gif>

[Accessed in 15 10 2017].

WHO, 2015. *Global Status Report on Road Safety 2015*. [Online]

Available at: http://www.who.int/violence_injury_prevention/road_safety_status/2015/en/

[Accessed in 25 07 2017].

Wikipedia, 2017. *ABS*. [Online]

Available at:

https://pt.wikipedia.org/wiki/Acrilonitrila_butadieno_estireno#/media/File:ABS_resin_formula.

PNG

[Accessed in 15 10 2017].

Wikipedia, 2017. *Acrylonitrile butadiene styrene*. [Online]

Available at: https://en.wikipedia.org/wiki/Acrylonitrile_butadiene_styrene

[Accessed in 15 10 2017].

Wikipedia, 2017. *Polycarbonato*. [Online]

Available at: <https://pt.wikipedia.org/wiki/Polycarbonato#/media/File:Lexan.svg>

[Accessed in 15 10 2017].

Appendix A

Technical file from ABS
ABS HI100H

SolutionPartner



ABS HI100H

Injection Molding

Description

High Impact, High Toughness

Application

Helmet, Pipe & Fittings

Properties	Test Condition	Test Method	Unit	Typical Value
Physical				
Specific Gravity		ASTM D792	-	1.02
Molding Shrinkage (Flow), 3.2mm		ASTM D955	%	0.4~0.7
Melt Flow Rate	220 °C/10kg	ASTM D1238	g/10min	10
Mechanical				
Tensile Strength, 3.2mm @ Yield	50mm/min	ASTM D638	kg/cm ²	390
Tensile Elongation, 3.2mm @ Break	50mm/min	ASTM D638	%	30
Tensile Modulus, 3.2mm	1mm/min	ASTM D638	kg/cm ²	17,200
Flexural Strength, 3.2mm	15mm/min	ASTM D790	kg/cm ²	630
Flexural Modulus, 3.2mm	15mm/min	ASTM D790	kg/cm ²	20,000
IZOD Impact Strength, 6.4mm (Notched)	23 °C	ASTM D256	kg-cm/cm	43
	-30 °C		kg-cm/cm	29
IZOD Impact Strength, 3.2mm (Notched)	23 °C	ASTM D256	kg-cm/cm	50
	-30 °C		kg-cm/cm	31
Rockwell Hardness	R-Scale	ASTM D785	-	93
Thermal				
Heat Deflection Temperature, 6.4mm (Unannealed)	18.6kg	ASTM D648	°C	86
	4.6kg		°C	89
Vicat Softening Temperature	5kg, 50 °C/h	ASTM D1525	°C	93
Flammability		UL94		HB
Relative Temperature Index		UL 746B		
Electrical			°C	60
Mechanical with Impact			°C	60
Mechanical without Impact			°C	60

ABS HI100H

Injection Molding

Description

High Impact, High Toughness

Application

Helmet, Pipe & Fittings

Electrical

Comparative Tracking Index(CTI)	Solution A	IEC 60112	Volts	0
Surface Resistivity		IEC 60093	Ohm	
Volume Resistivity	23℃	ASTM D257	Ohm·m	
Arc Resistance	23℃	ASTM D495	Ohm·cm	6

Note) Typical values are only for material selection purpose, and variation within normal tolerances are for various colors.

Values given should not be interpreted as specification and not be used for part or tool design.

All properties, except melt flow rate are measured on injection moulded specimens and after 48 hours storage at 23℃, 50% relative humidity.

Processing Guide (Injection Molding)

Processing Parameters		Unit	Value
Drying Temperature		℃	80
Drying Time		hrs	2 ~ 4
Minimum Moisture Content		%	0.01
Melt Temperature		℃	210 ~ 240
Cylinder Temperature	Rear	℃	180 ~ 200
	Middle	℃	190 ~ 210
	Front	℃	200 ~ 220
Nozzle Temperature		℃	200 ~ 230
Mold Temperature		℃	40 ~ 70
Back Pressure		kg/cm ²	300 ~ 600
Screw Speed		rpm	30 ~ 60

Note) Back Pressure & Screw Speed are only mentioned as general guidelines.

These may not apply or need adjustment in specific situations such as low shot sizes, thin wall molding and gas-assist molding.